Kondo effect in metallic glasses with Non-Fermi Liquid behaviors

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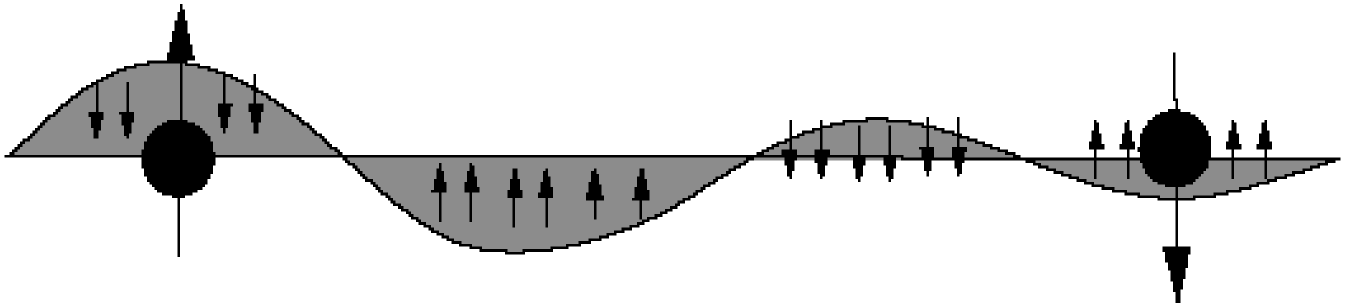
Introduction

RKKY interaction



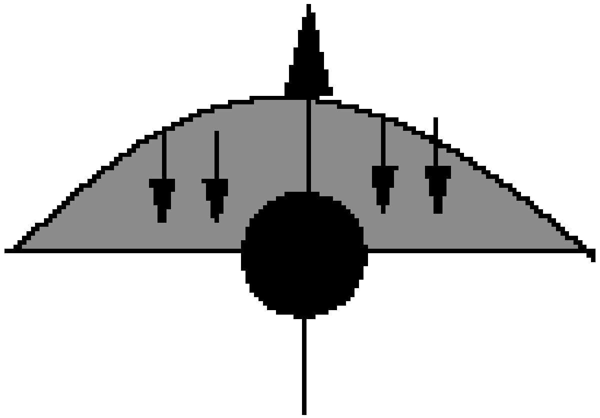
Exchange interaction between two localized moments via the conductive electrons

$E_{RKKY} \propto N(E_F)J^2$,

J is exchange interaction constant

Kondo interaction: hybridization of *f* and conductive electrons

Kondo interaction



Exchange interaction b/n magnetic moment and spin of conductive electron

$$k_B T_k \propto \exp[-1/N(E_F)J]$$

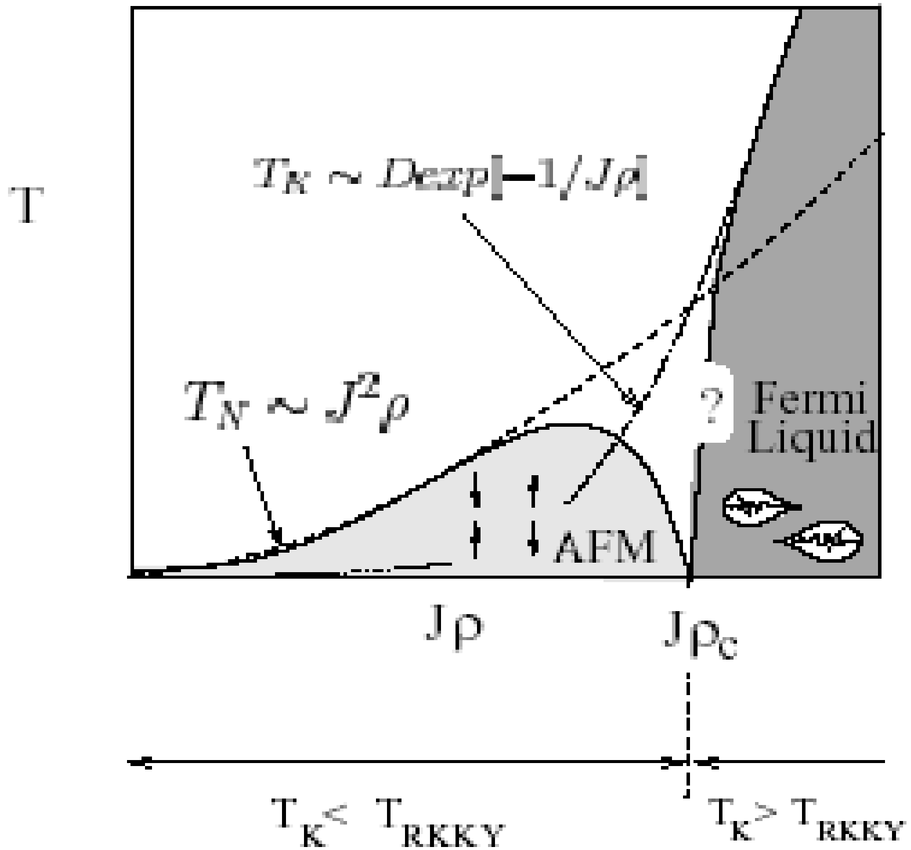
（J<0）

T_K is characteristic temperature of Kondo system

Kondo effect is often observed in alloys with local electrons well below the Fermi surface and very dilute local moments. Systems with deeply localized moments often perform a magnetic order behavior at low T that is dominated by direct interaction of local spins or by RKKY interaction if local spins are dilute.

Kondo effect remains an active area in condensed matter physics

Competition between Kondo effect and RKKY interaction

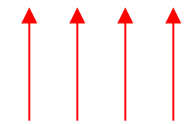


$T_K < T_{RKKY}$: **Antiferromagnetic regime;**

$T_K > T_{RKKY}$, **HF regime**

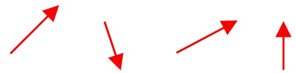
Exchange Interaction energy

$E_M = -JS_1 \bullet S_2$



Thermal energy

$E_T = k_B T$



Heavy Fermion (HF)= strong e-e correlation

The moments (*f* electrons) combine with the conduction electrons to form very heavy quasiparticles, with masses that are two to three orders of magnitude larger than the mass of the free electron

The Kondo interaction b/n *f* (*d*) electron and conduction electron induces HF

Found in 1975

C_p is very effective method to study e-e interaction

$\gamma \geq$ 400 mJ/mole K^2 is HF

$$C_p=\gamma T+\beta T^3$$

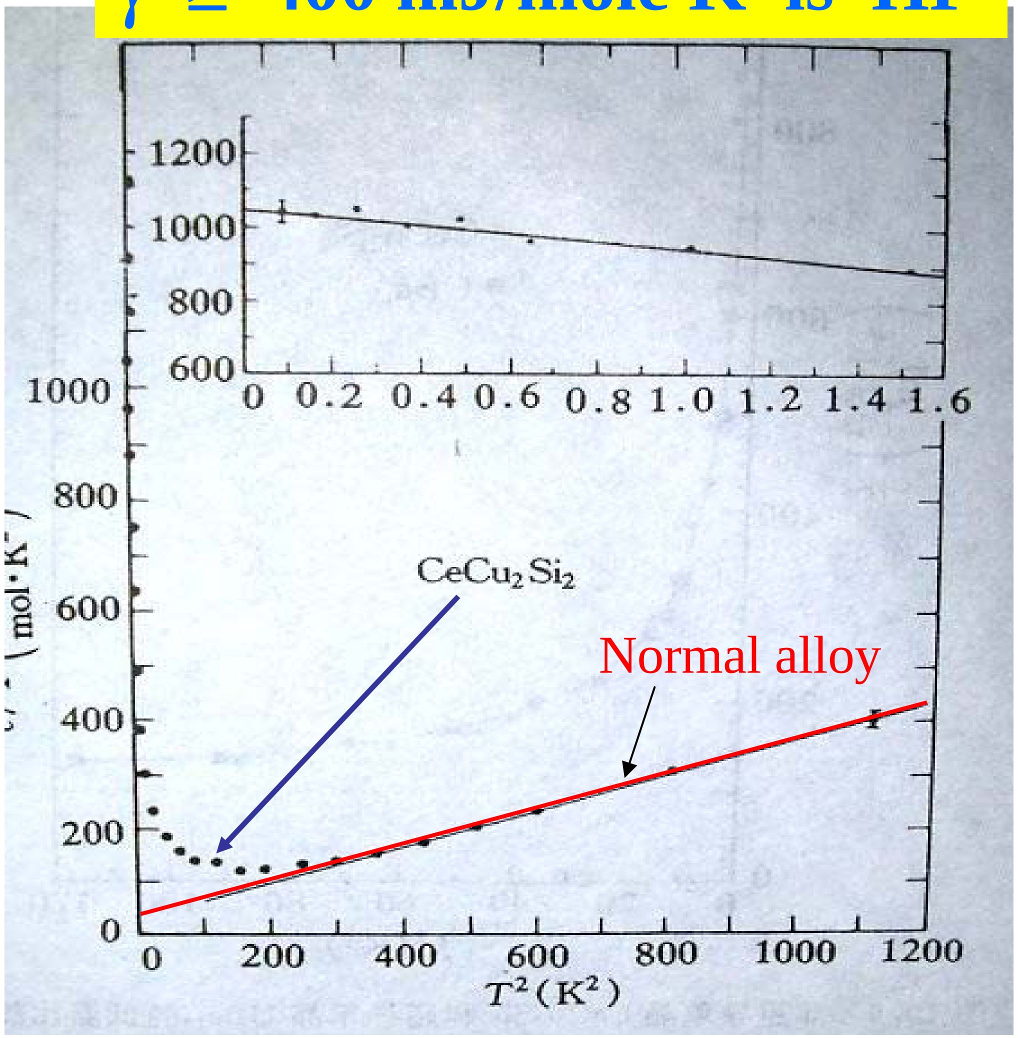
$$C_p/T=\gamma+\beta T^2$$

$$\gamma=m^* k_F k_B^2/3h^2,$$

m* **= effective mass of electron**

For normal metals,

$\gamma \leq$ 10 mJ/mole K^2



CeAl crystalline alloy, γ=1600

Specific heat

Some typical HF systems

Table 3.5. Key Parameters of Some Single Crystal Heavy Fermion Compounds: T_N the Néel Temperature, T_c the Superconducting Transition Temperature and T_{sf} the Spin Fluctuation Temperature (after van Dijk^{+} [58], and Aeppli and Broholm [59]).

Compound	γ (mJ/mol.K^2)	μ_{at}/μ_B	T_N (K)	T_c (K)	T_{sf} (K)
$CeCu_6$	1600				
$CeInCu_2$	1200	0.4	2.0	0.46	
UBe_{13}^{+}	1100			0.9	5
$CeCu_2Si_2^{+}$	1000		0.6	0.6	5
U_2Zn_{17}	535	0.81	9.7		
$UPt_3^{(+)}$	450	0.02	5–6	0.5^{+}	30^{+}
$CeRu_2Si_2$	385				
$CeInSn_2$	270				
CeNiSn	200				
TmSe	350	1.7	3.2		
URu_2Si_2	60^{+}	0.04	17.5	1.2^{+}	70^{+}

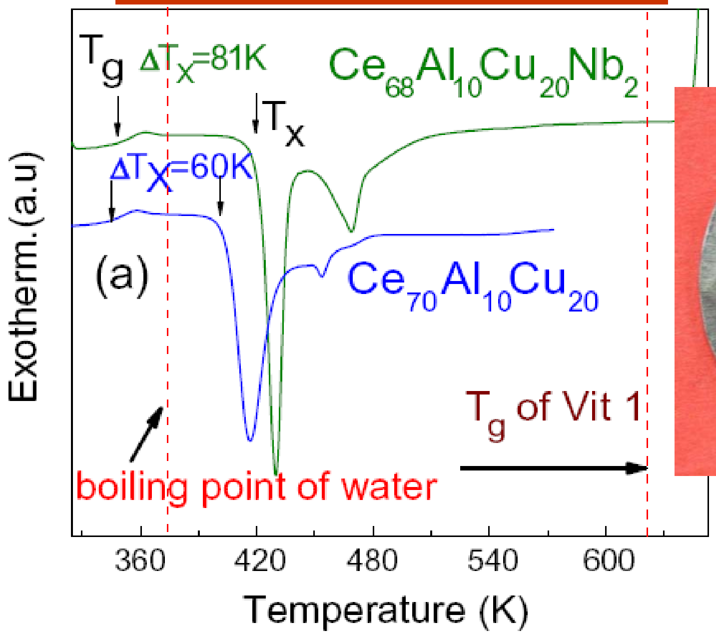
HF systems are usually crystalline Ce & U alloys

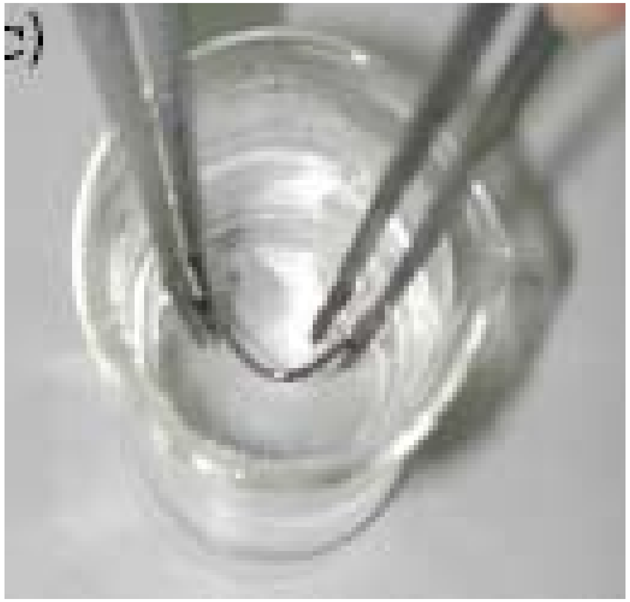
- **Kondo behavior was only studied in crystalline compounds & ordered alloys. Is there Kondo effect and HF behavior in strongly disordered alloys?**

- **The role of disorder in Kondo effect & HF behavior, and the interplay of disorder and strong correlations remains one of the least understood topics of condensed matter physics.**

- **Disorder effects are important for the understanding of the puzzling non-Fermi-liquid(NFL) behavior**

Ce based BMGs





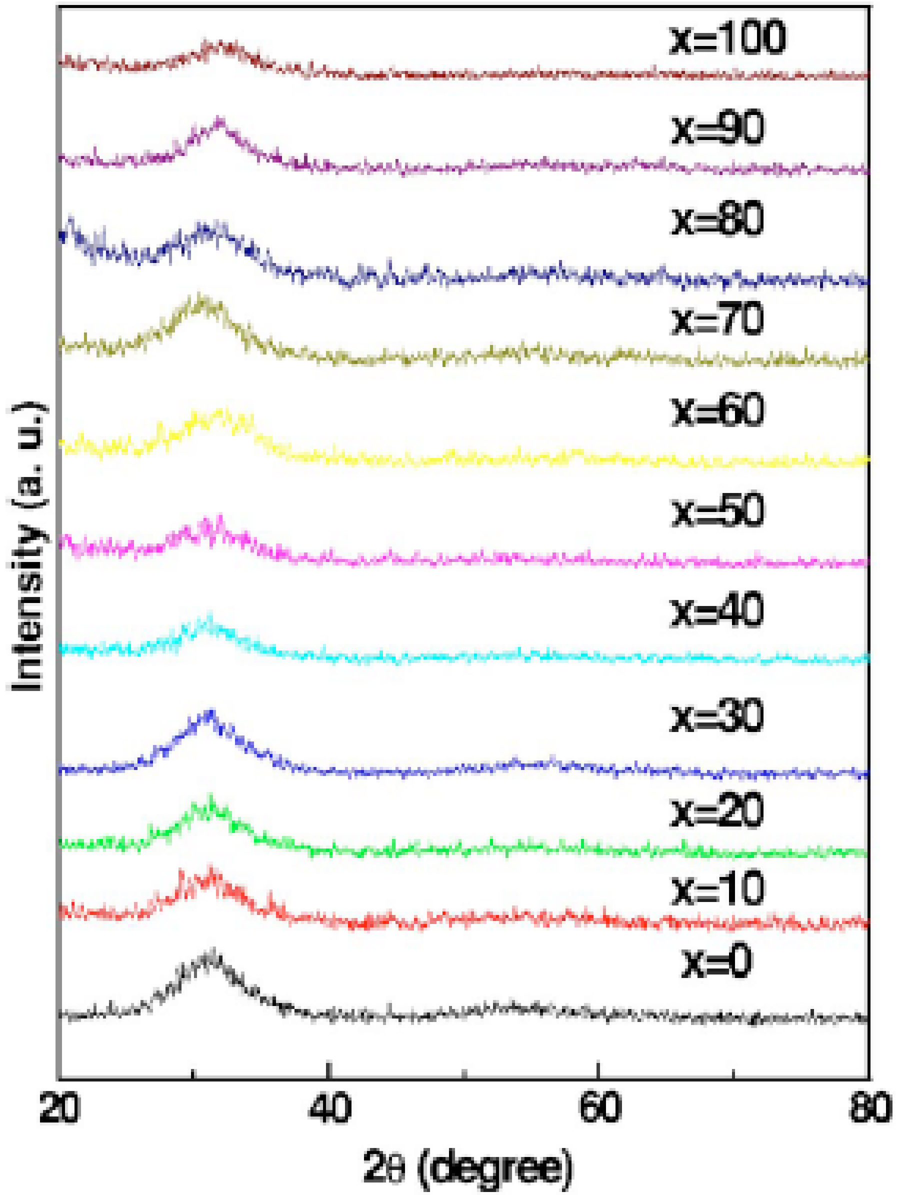
- □ **Maximum diameter ~ 20 mm**
- □ **Wide composition range**
- □ **Strong structural disorder**
- □ **Tunable composition & dis-ordering**

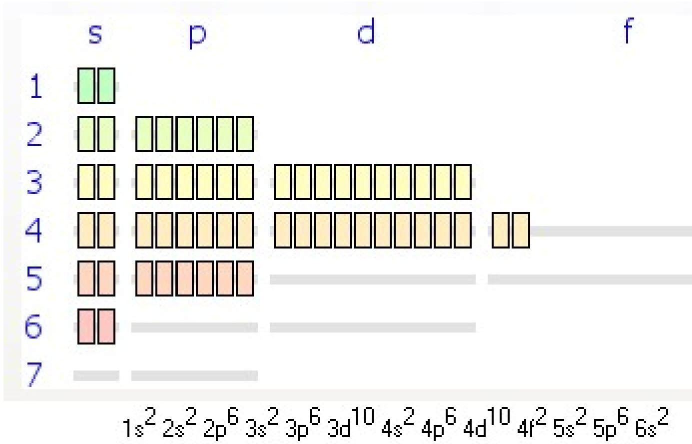
PRL 94, 205502(2005)

Motivation

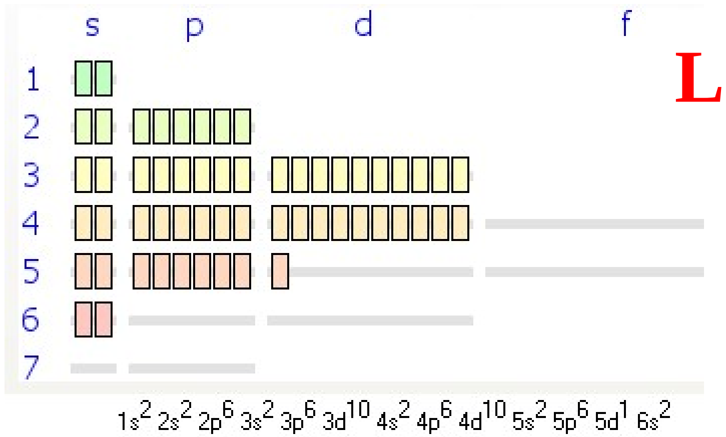
- **Study Kondo effect & HF in strongly disordered Ce-based glass alloys**
- **Effects of structural disorder on Kondo effect & HF**
- **Minor addition can induce giant physical properties changes in BMGs, along this idea, to develop new BMGs with Kondo effect, and provide new model system to study the Kondo effect and NFL**

Kondo effect and HF behavior in Ce-BMGs





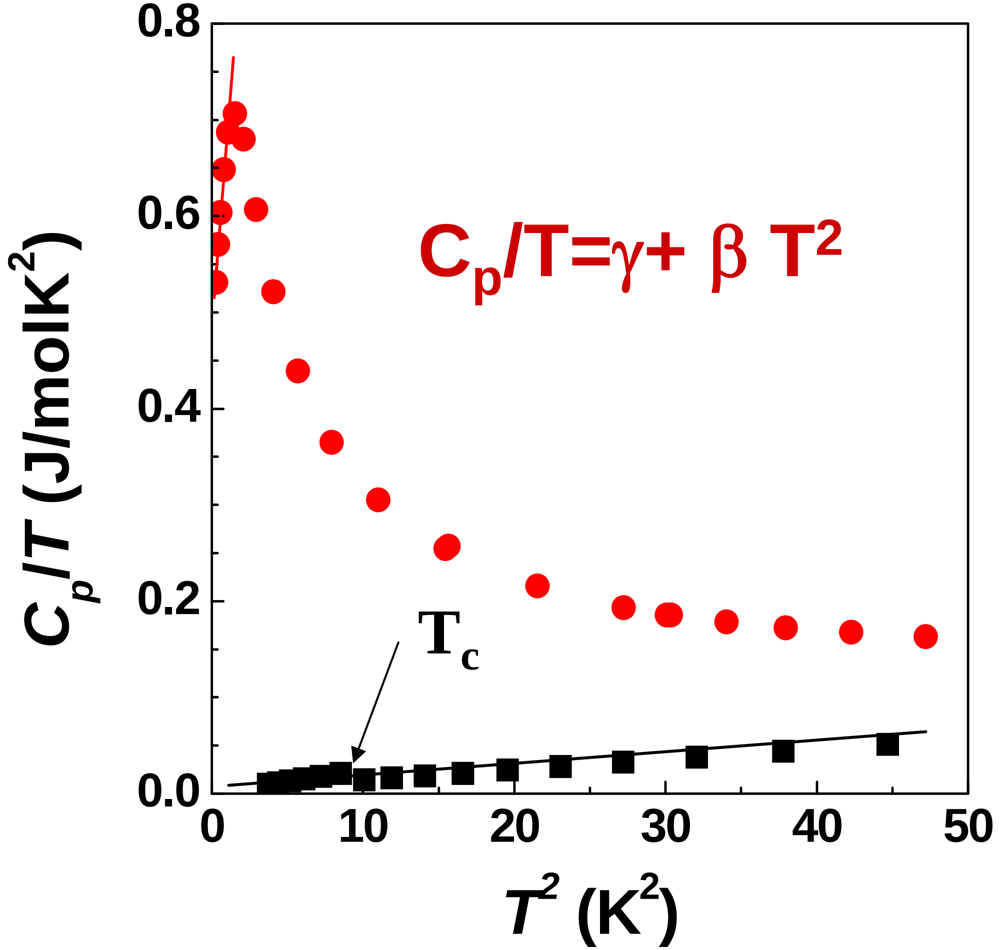
Ce



La

$(Ce_xLa_{1-x})_{65}Al_{10}Cu_{20}Co_5$

Low-T C_p of CeLa-based BMGs



$Ce_{65}Al_{10}Cu_{20}Co_5$ BMG

Larger γ value

Nonmagnetic

$La_{65}Al_{10}Cu_{20}Co_5$ BMG

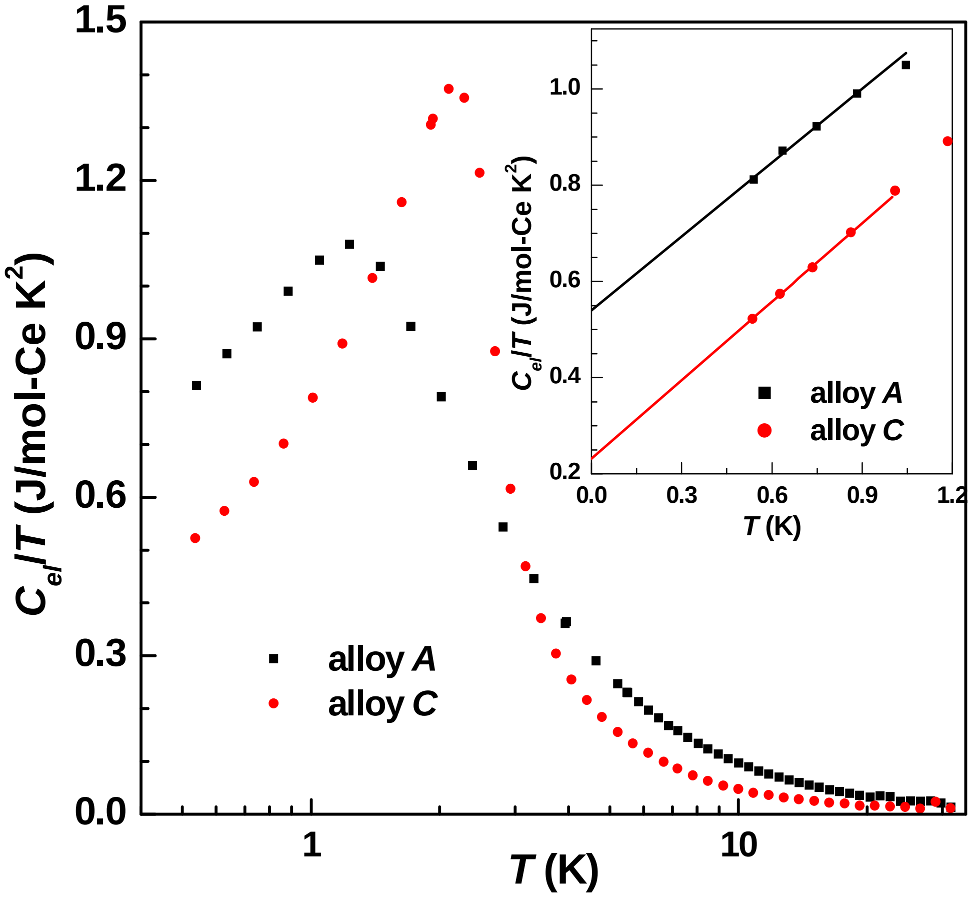
Smaller γ value

γ=3.4 mJ/mol K^2

$$C_p=\gamma T+\beta T^3$$

$$C_p/T=\gamma+\beta T_2$$

$$\gamma=m^*k_F k_B{}^2/3h^2$$



C_{el} normalized to a mole of Ce was obtained by subtracting Cp of La-BMG

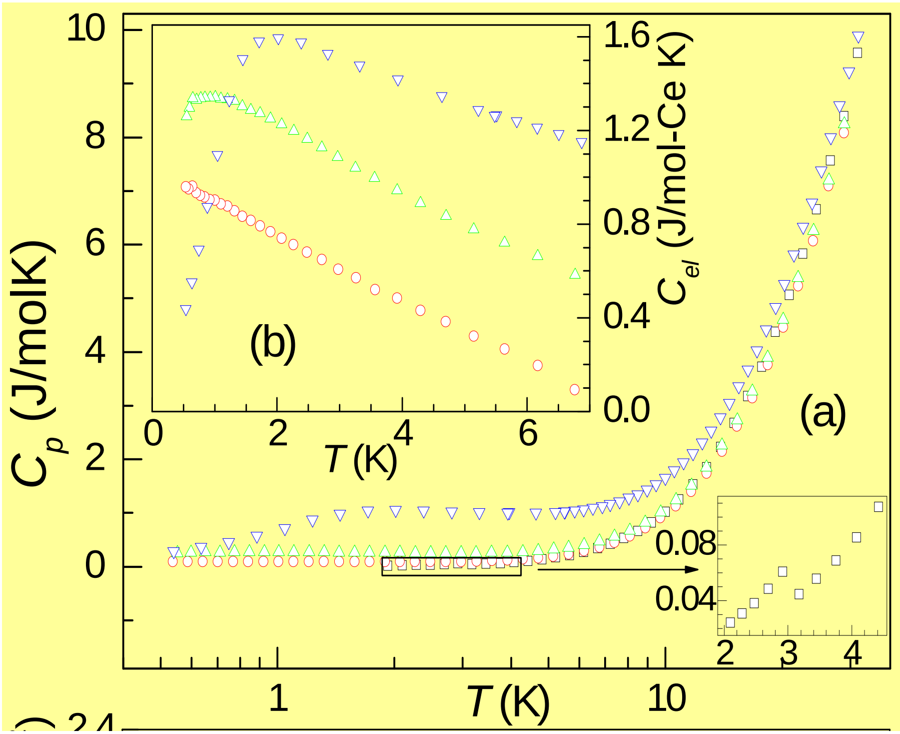
The broad peak in C_{el}/T is spin-glass-like effect at very low-T induced by disordered arrangement of localized moments in the high Ce-content glass.

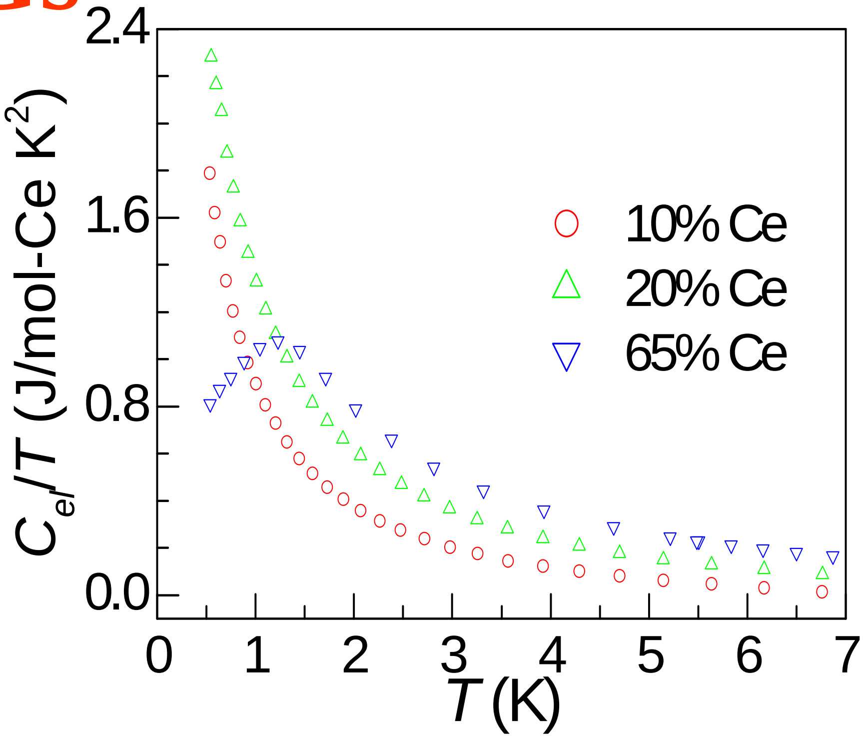
Alloy A: $Ce_{65}Al_{10}Cu_{20}Co_5$ BMG
γ=811 mJ/mol K^2

Alloy C: Crystallized $Ce_{65}Al_{10}Cu_{20}Co_5$ BMG
γ=501 mJ/mol K^2

Heavy electron BMGs

PRB 75, 172201 (2007)

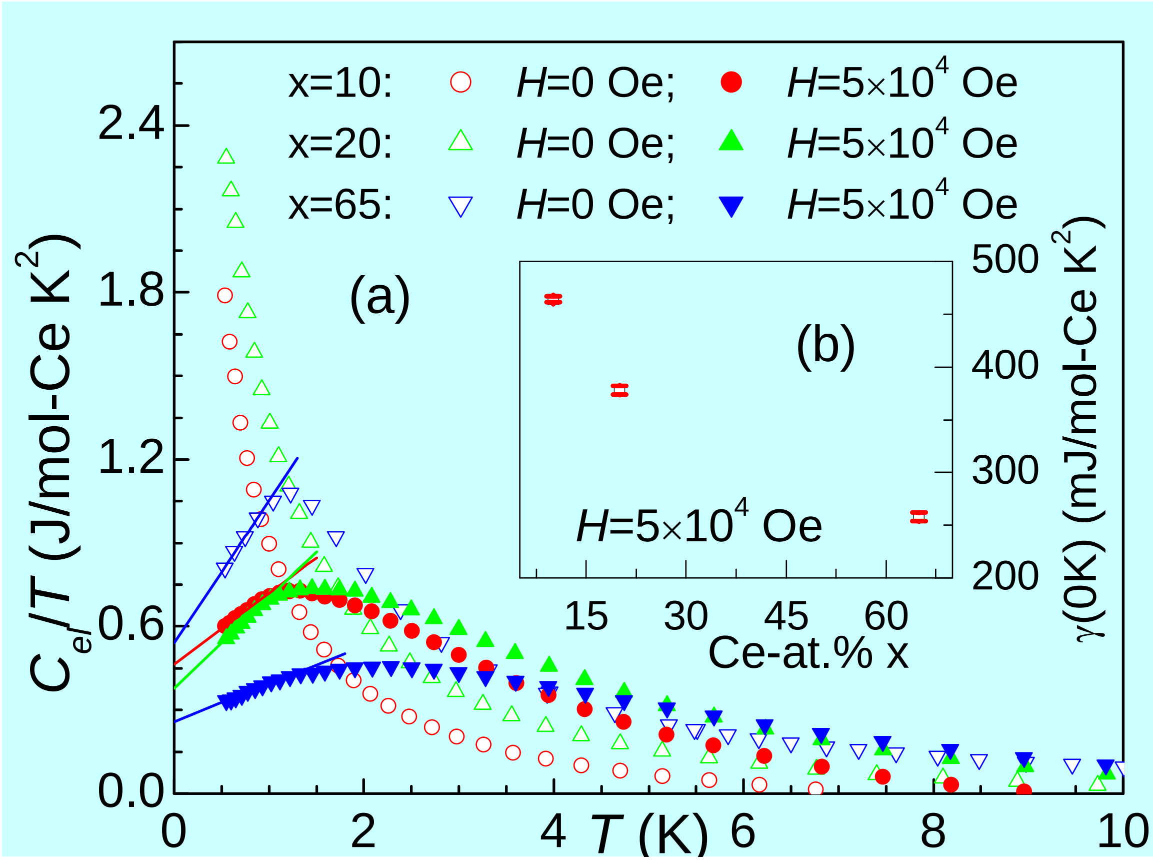




γ (0.53 K) for $Ce_xLa_{65-x}Al_{10}Cu_{20}Co_5$ BMGs with x=10, 20 and 65 are 1789, 2282 and 811 mJ/mol-Ce·K^2

The enormous γ indicates that the BMGs behave as a HF alloy, which is due to the competition b/n Kondo effect and RKKY interaction

Under magnetic field



At $5x10^4$ Oe: For glass *x*=65, γ=258 mJ/mol Ce K^2. For glass *x*=10: γ =464 mJ/mol Ce K^2. The large γ remaining in high H further confirms that the glasses are HF alloys, and the HF behavior can be tuned by H

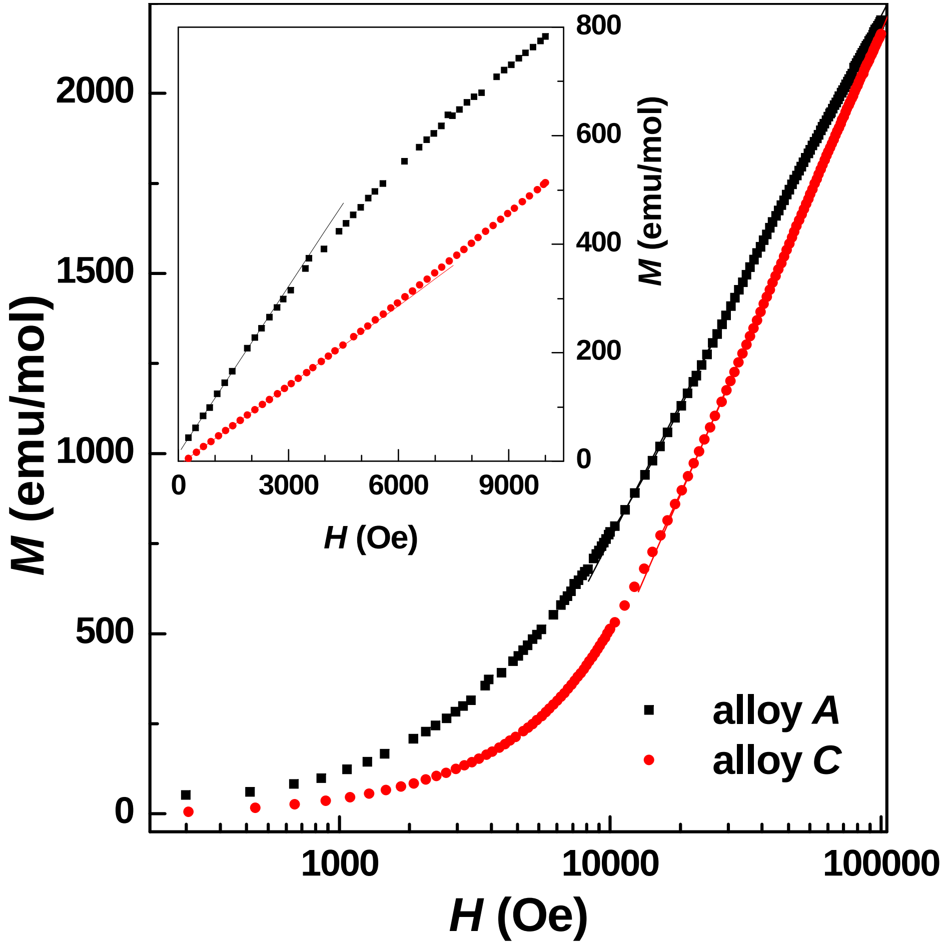
Fermi liquid(NL) and Non-Fermi liquid(NFL)

Difference in physical properties

	FL	NFL
Resistance	$R=R_0+AT^2$	$R=R_0+AT^\alpha$
Specific heat of electron	$C/T \sim \gamma$ (constant）	$C/T \sim -lnT$
Magnetic susceptibility	$\chi \sim$ constant	$\chi \sim -lnT$

Some Ce compounds exhibit FL behavior

Magnetization at 1.9 K



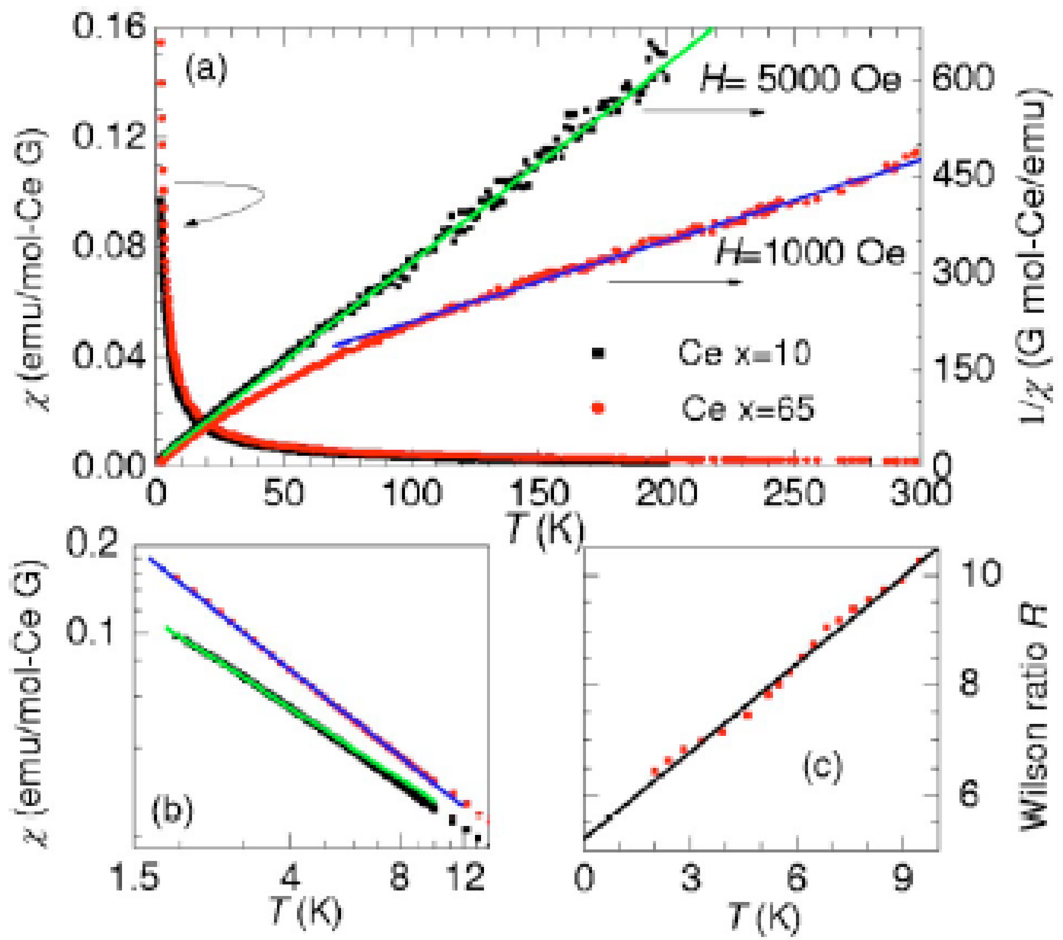
At high magnetic field *H*: $M \propto \ln H$

At low *H*: $M \propto H$

Fit the disorder-induced Griffiths phase spin cluster model:

the magnetization is predicted to exhibit low-field behavior ($M \propto H$), which cross over to the respective high-field behavior ($M \propto H^{\lambda}$)

Low-T susceptibility



$Ce_xLa_{65-x}Al_{10}Cu_{20}Co_5$ BMGs

At high T (23 K ~250 K) : $\chi \propto \frac{1}{T+\theta}$

Curie-Weiss law (θ=80.5; μ_{eff}=2.53 for x=65) μ_{eff}: theoretical value for Ce: 2.54

At low T: $\chi \propto T^{-1+\lambda}$

λ =0.0041 (*x*=65) and 0.1874 (x=10), which is in agreement with the prediction of the Griffiths phase model, indicating that the HF systems show NFL behavior

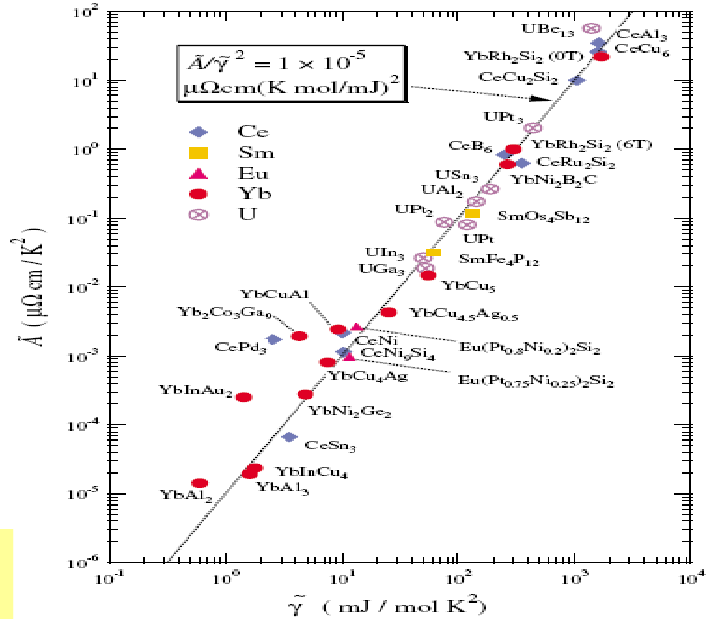
$$A/\gamma^2 = 1.0\times10^{-5}\,\mu\Omega cm(Kmol/mJ)^2$$

A is coefficient T^{α} term in resistivity

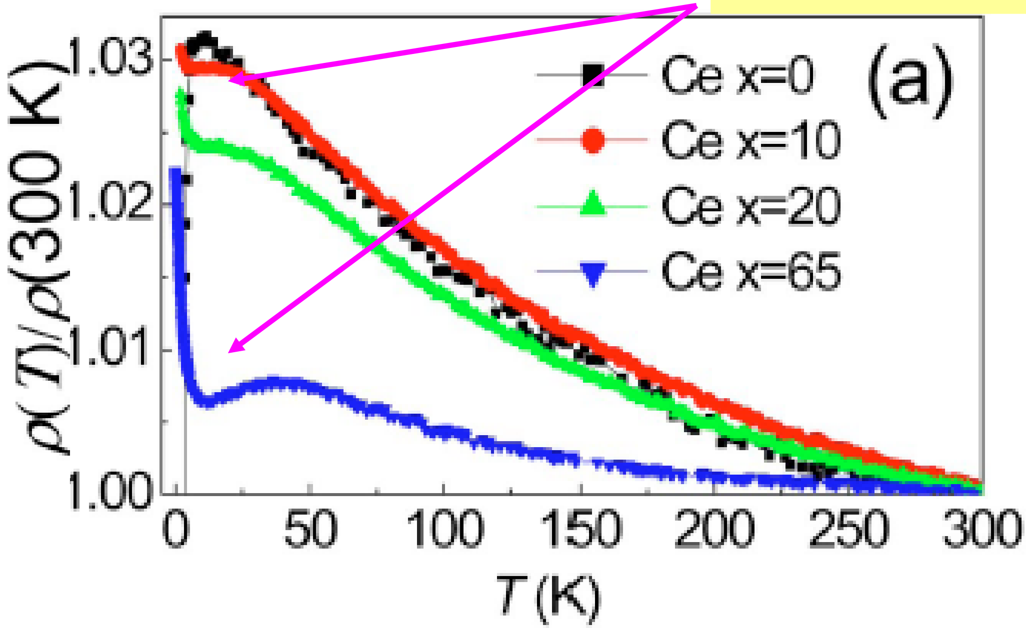
$$\rho=\rho_0+AT^{\alpha}$$

For many *f*-electron HF systems, exist a universal value of Kadowaki-Woods relation A/γ^2 : 1×10^{-5} $\mu\Omega$ cm (K mol/mJ)^2

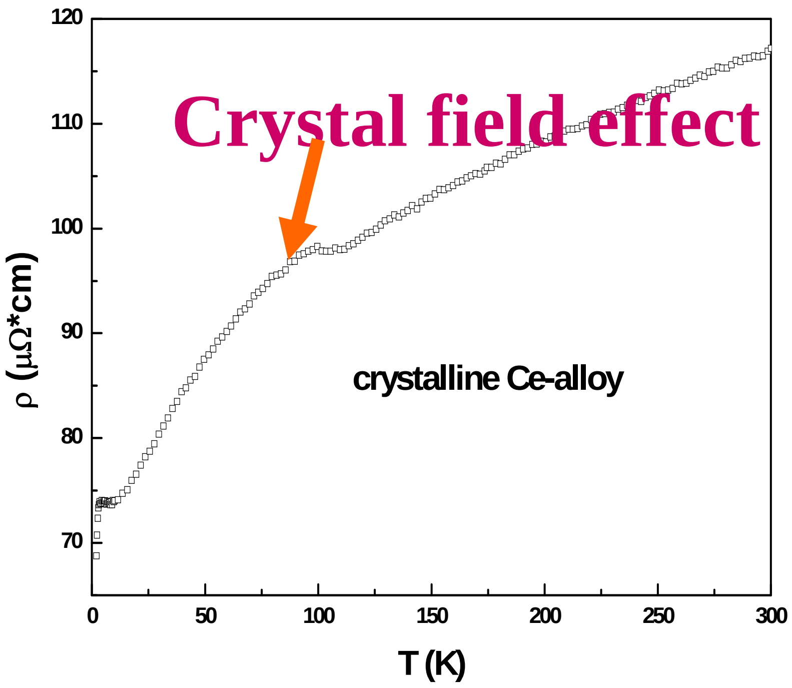
Phys. Rev. Lett. **94**,57201 (2005)



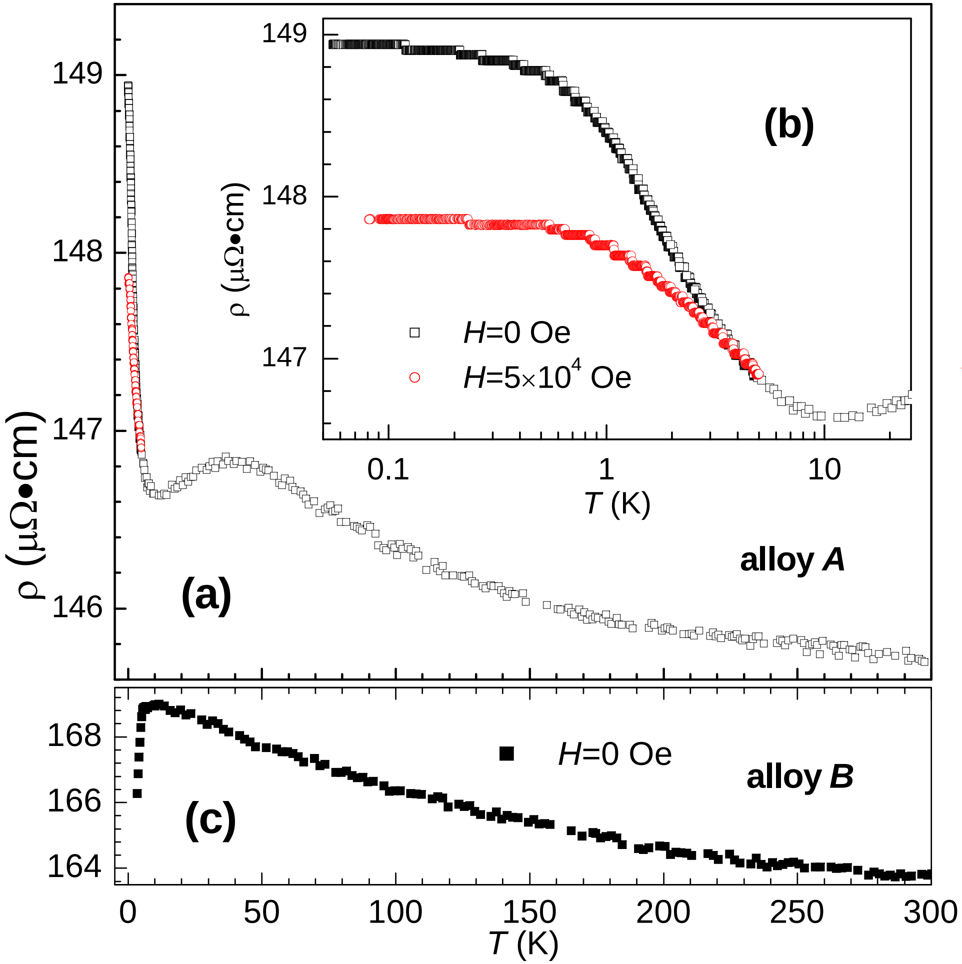
Kondo effect



$Ce_xLa_{65-x}Al_{10}Cu_{20}Co_5$ BMGs



Low-T resistivity



$\rho = \rho_0 + AT^{\alpha}$ with A=-0.537

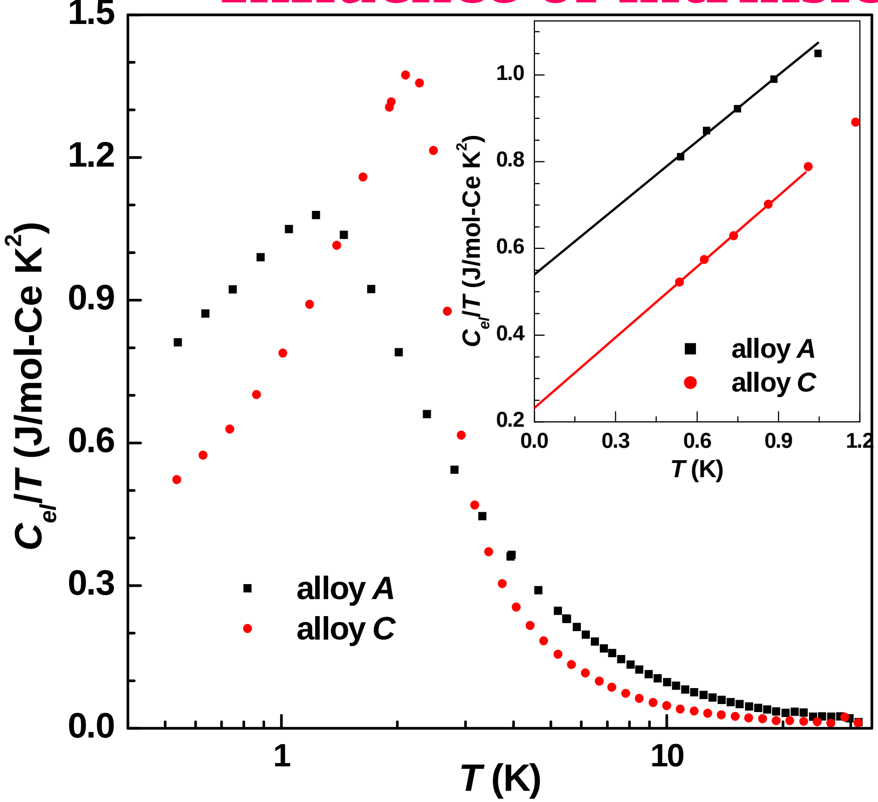
A/γ^2 is about 0.8×10^{-5} μΩ·cm (K mol-Ce/mJ)^2 for alloy *A*, which is close to the universal value and confirms HF systems show NFL behavior

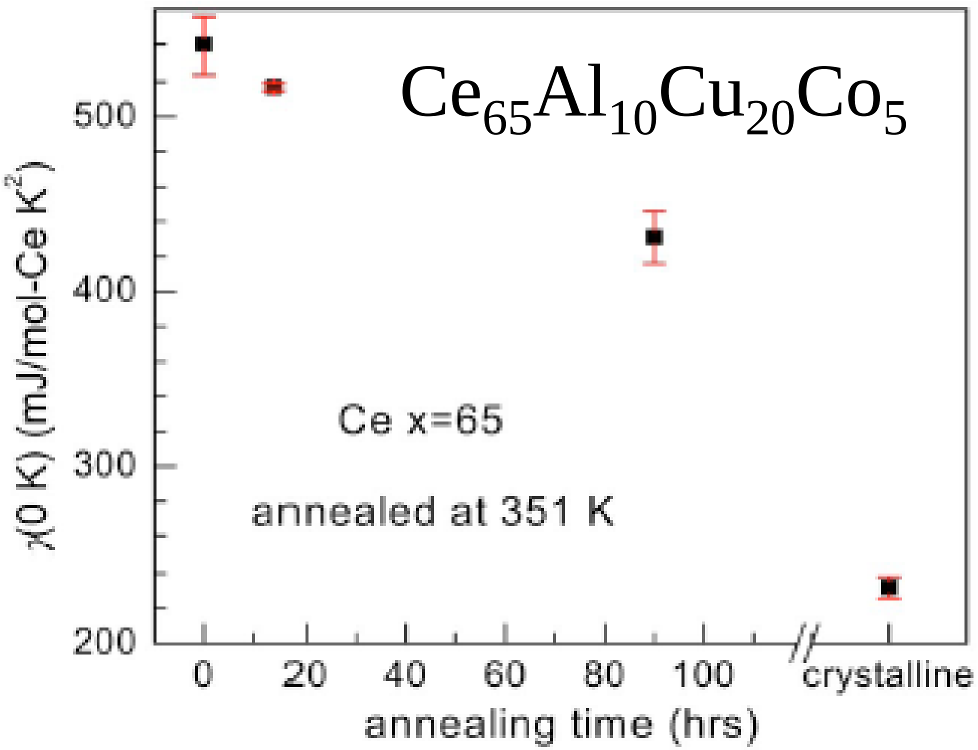
Alloy A: $Ce_{65}Al_{10}Cu_{20}Co_5$ BMG

PRB 75, 172201 (2007)

Alloy B: $La_{65}Al_{10}Cu_{20}Co_5$ BMG

Influence of intrinsic structural Disorder on HF





BMG: HF behavior → Crystallized BMG "light" non-fermion behavior): disorder induced HF behavior.

γ is decreased with the ordering of the BMG and it is much decreases when BMG is crystallized

PRB 75, 172201 (2007)

In a simple picture the coupling constant, Γ depends on the energy levels

$$\Gamma = N(E_F)V^2 / (E_f - E_F)$$

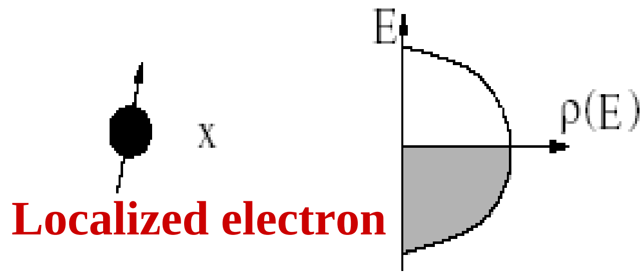
$N(E_F)$ is the Fermi density of states,

V is hopping matrix between conduction band and f-level

E_f the energy of f-level; E_F the Fermi energy

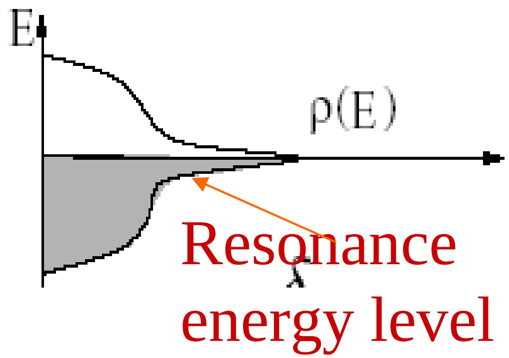
$T_k \propto exp(-1/\Gamma)$.

energy band of conductive e



Before hybridization

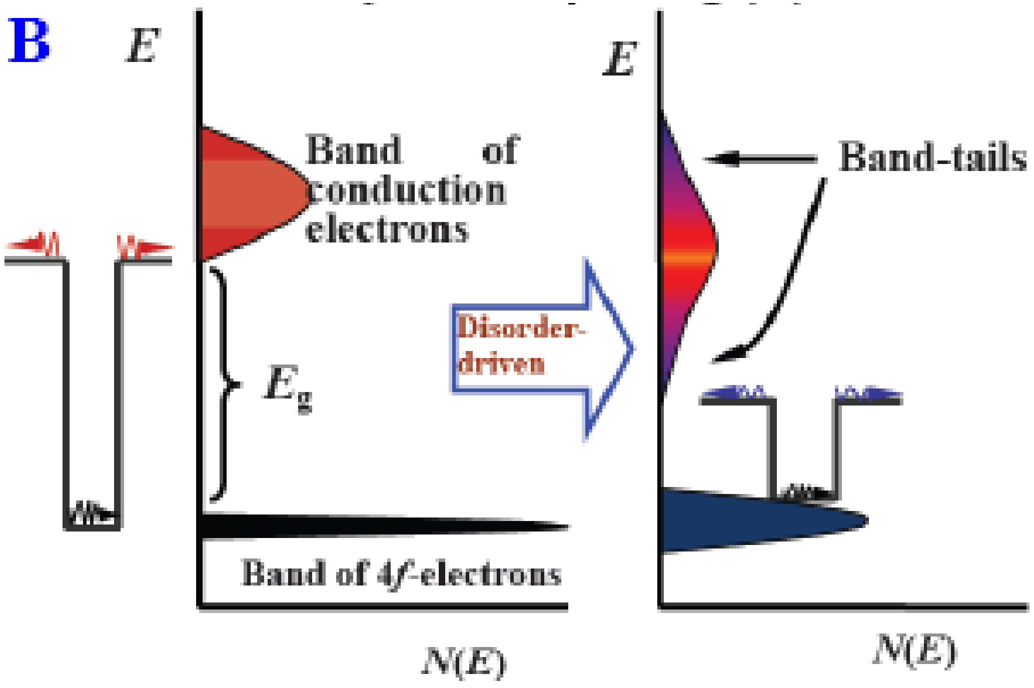
In BMG, the distribution in the local volume, or atomic-level pressure results in the distribution in conductor electron and f-levels, and thus decrease of Γ factor.



RKKY interaction is roughly proportional to Γ^2

After hybridization

Possible reasons for HF behavior in BMG

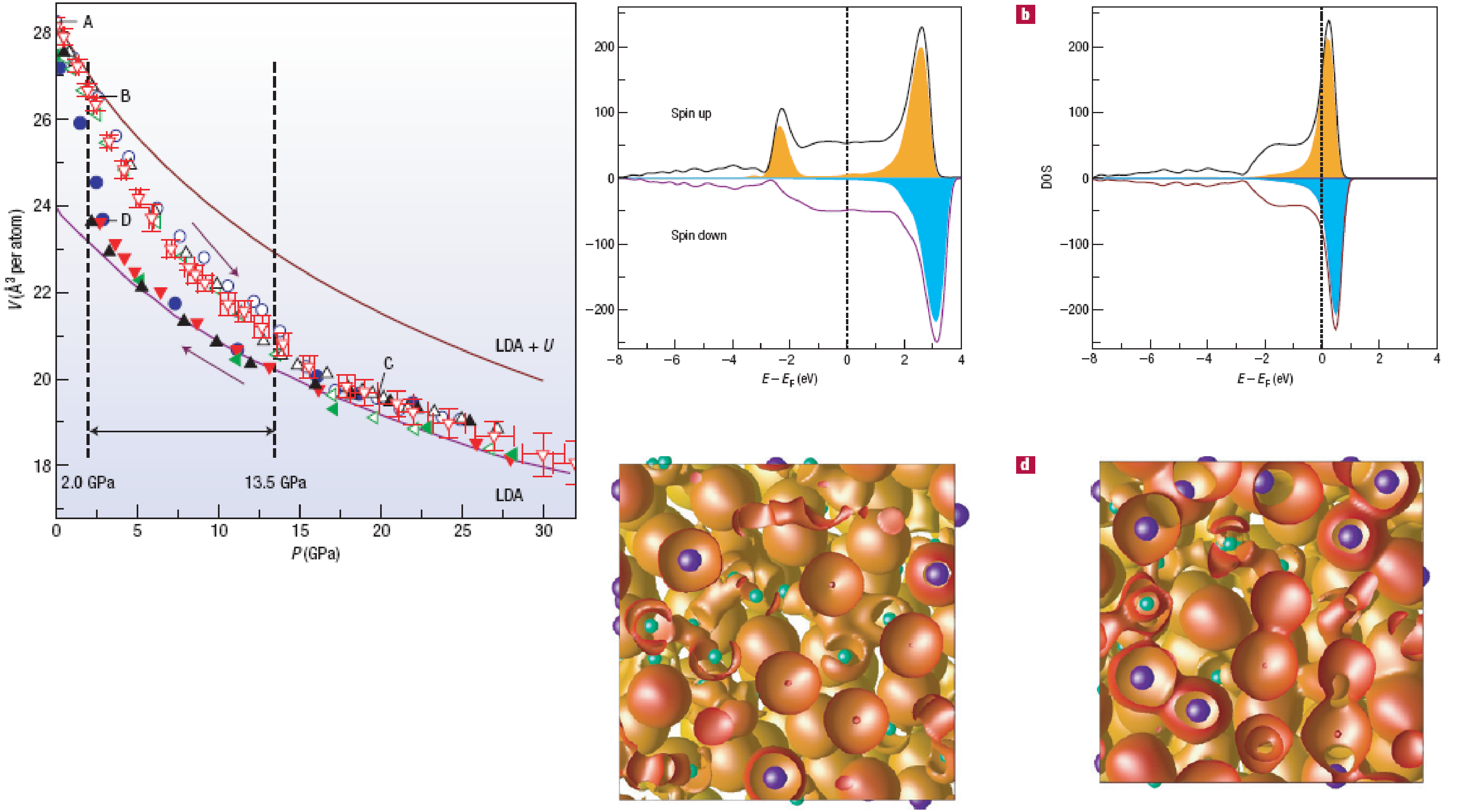


For BMG, heavy "band-tails" deriving from the spatial disorder are introduced into the conduction band , and the band of localized *f* electrons is extended and also possesses large density of states.

The depth of energy-trap decreases after being made glassy, possibility of *f* e to get out trap increase

Disorder induced localized-itinerant *f* electron transitions

Along the idea, new glassy alloys containing rare earth elements might be developed to show Kondo effect



Pressure can induced localized-itinerant *f* electron transitions

H.W. Sheng, E. Ma et al, Nature Mater 6, 192 (2007)

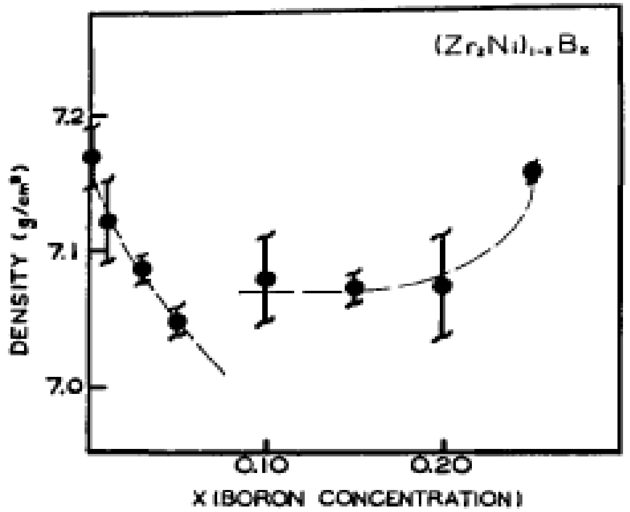
Kondo effect induced by micro alloying in BMGs

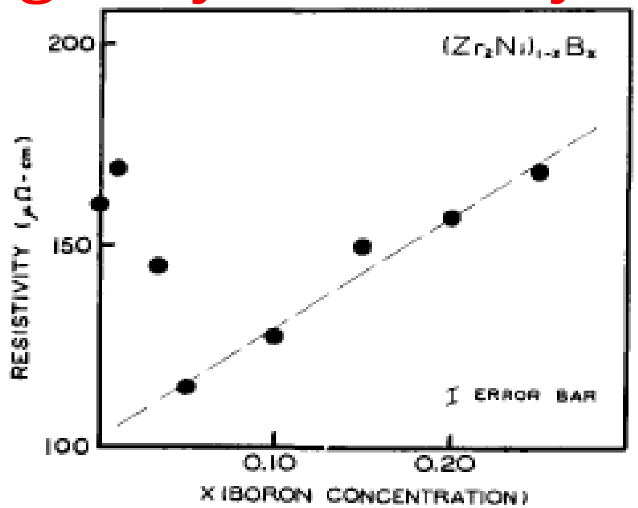
Effects of microalloying in BMGs

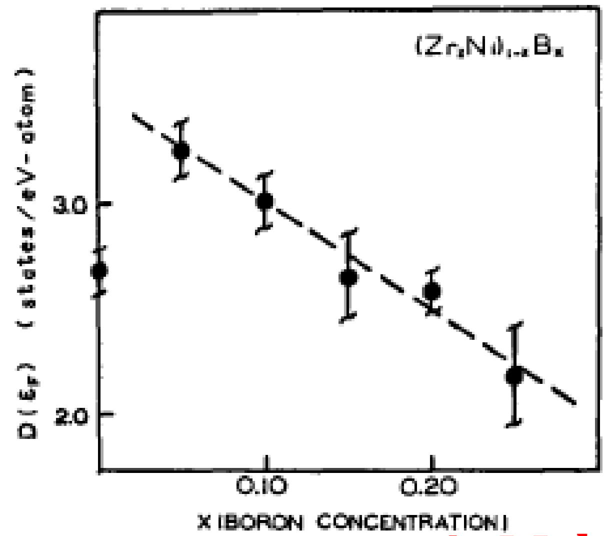
1. Enhance glass-forming ability (GFA)
2. Improve mechanical properties
3. Induce & tune physical properties
4. Influence relaxation, diffusion and glass transition
5. Form composites

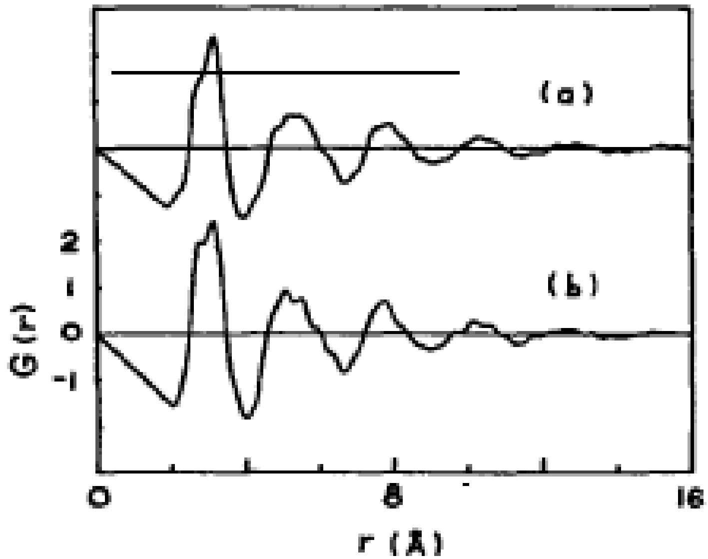
Prog. Mater Sci. 52 (2007) 540

Density, structure, electrical transport, DOS at Fermi surface, superconductivity of glassy $(Zr_{66.7}Cu_{33.3})_{1-x}B_x$ $(0 \leq x \leq 0.25)$ are significantly changed by microalloying.





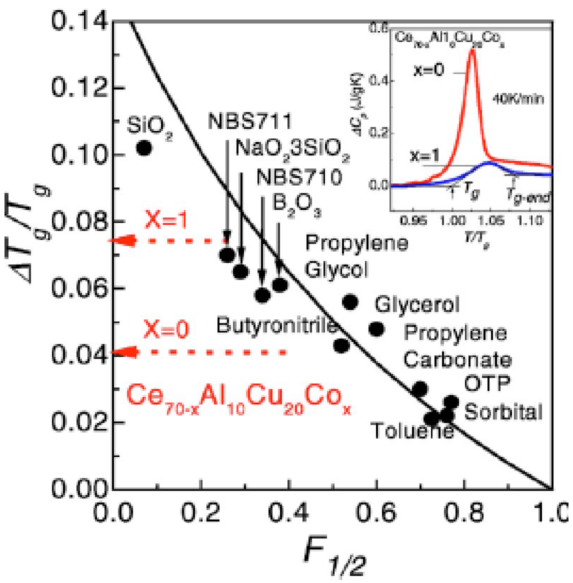




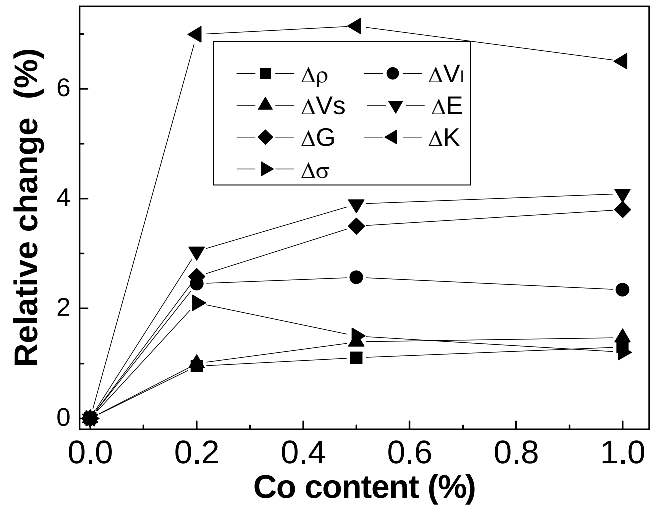
A. Mak, K Samwer, W.L. Johnson, Phys Lett A 98 (1983)

B Zhang PRB 73, 092201(2006)

W.L. Johnson, PRL, 92 (2004)

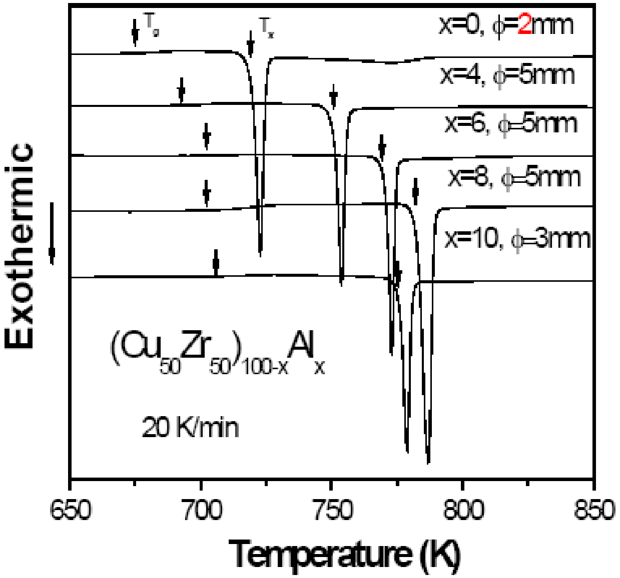


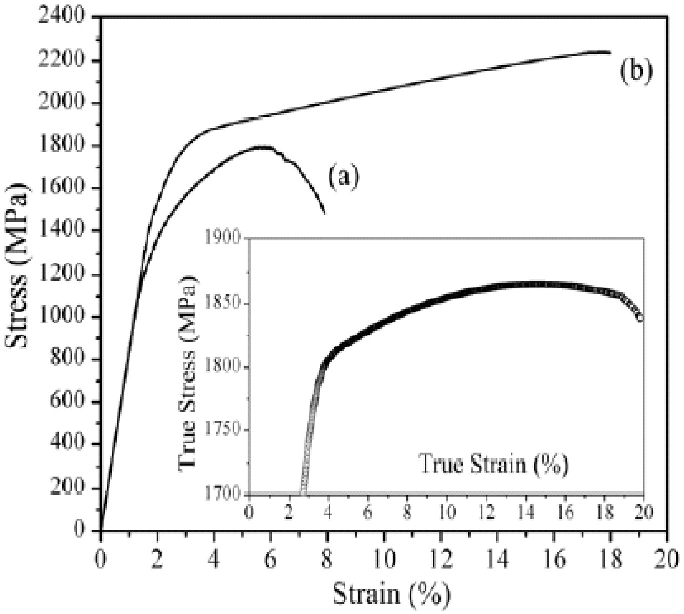
Alloy Composition(in at. %)	Critica
$Cu_{46}Zr_{54}$ [b]	2
$Cu_{46}Zr_{47}Al_7$	3
$Cu_{46}Zr_{45}Al_7Y_2$	8
$Cu_{46}Zr_{42}Al_7Y_5$	10
$Cu_{46}Zr_{37}Al_7Y_{10}$	4



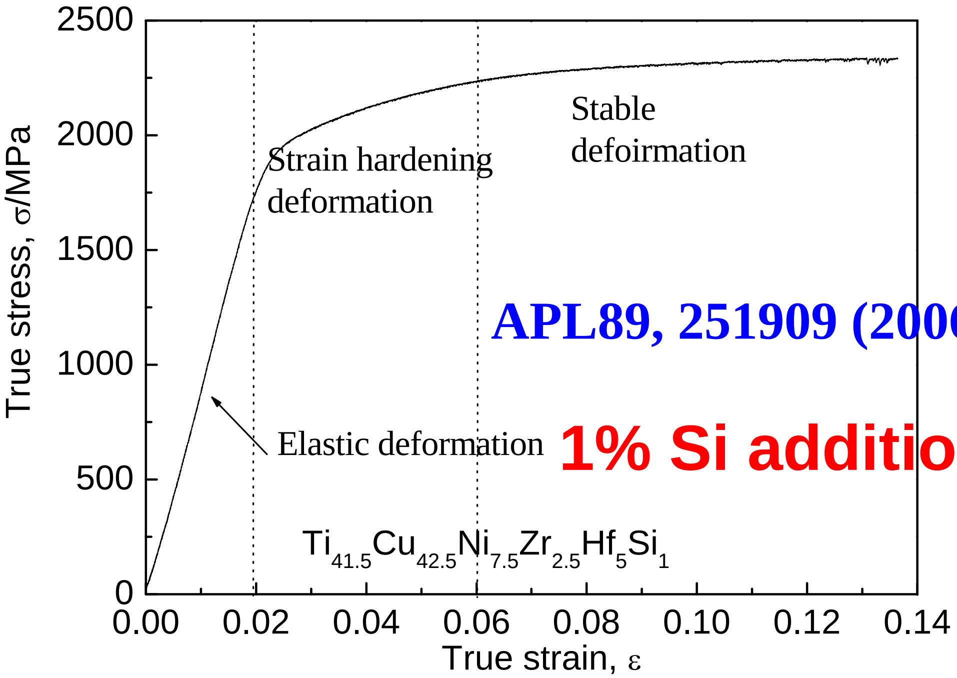
Ce-based BMGs

Plasticity in $(Cu_{50}Zr_{50})_{1-x}Al_x$ BMGs





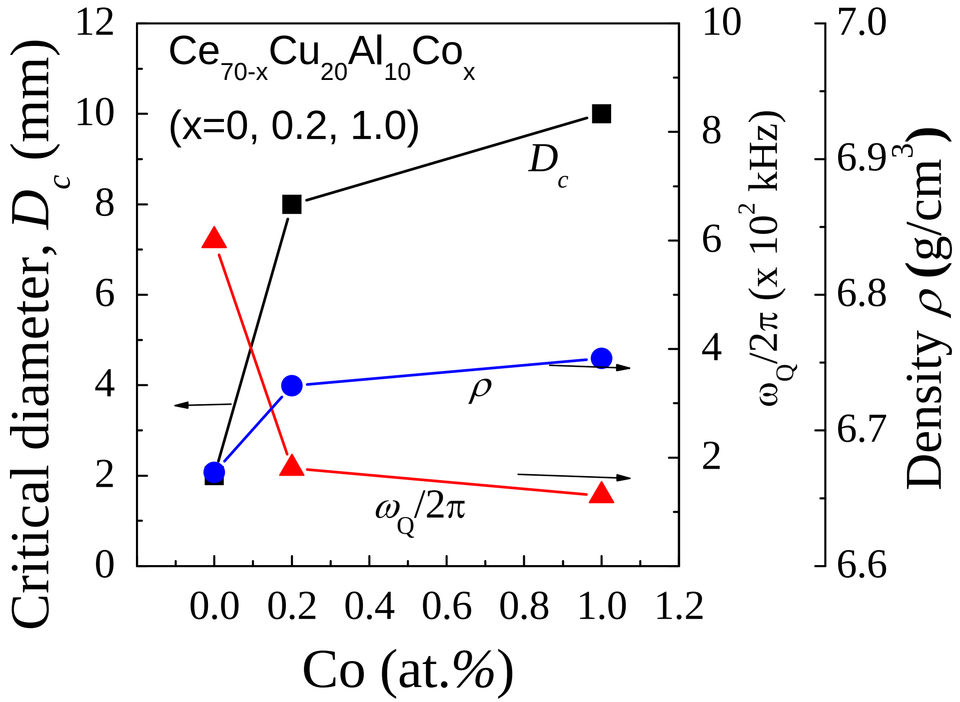
PRL, 94 205501(2005)

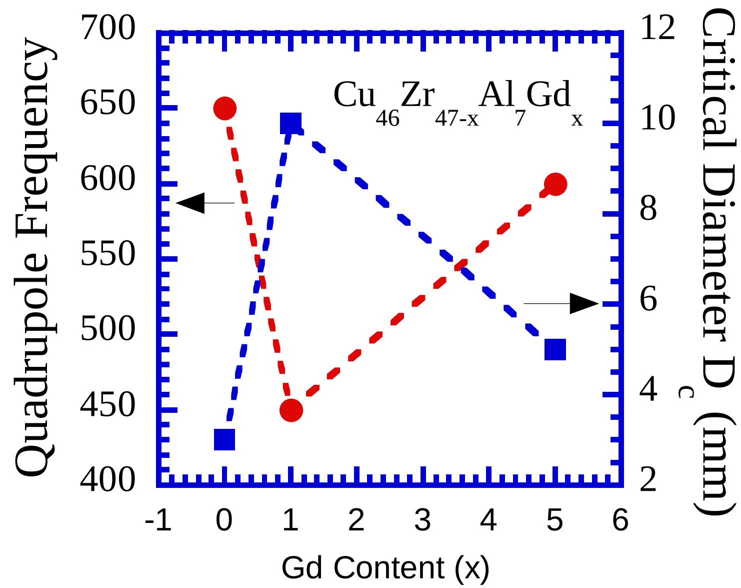


APL89, 251909 (2006)

1% Si addition

High GFA corresponds to weak quadrupole interaction!





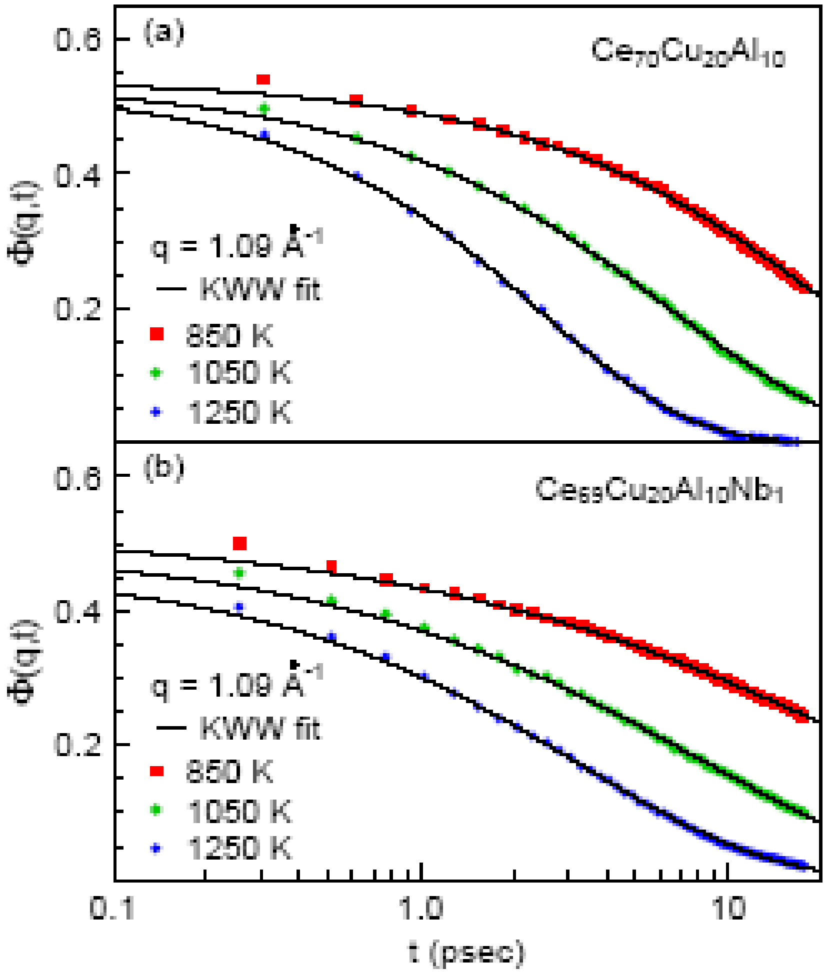
Improved site symmetry favors higher GFA.

Correlation between GFA and local geometry

Structural change is the origin of microalloying!

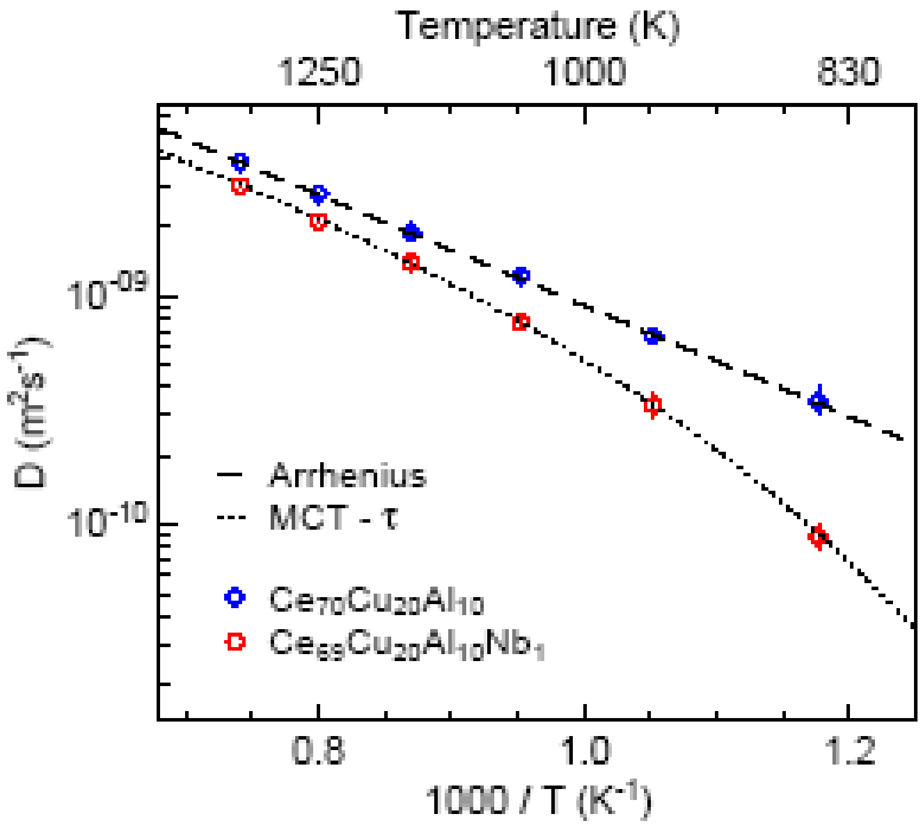
Xi et al, Phys. Rev. Lett. 99, 095501 (2007)

Dynamic change $Ce_{69}Cu_{20}Al_{10}$ with Nb_1 K. Samwer APL 2009

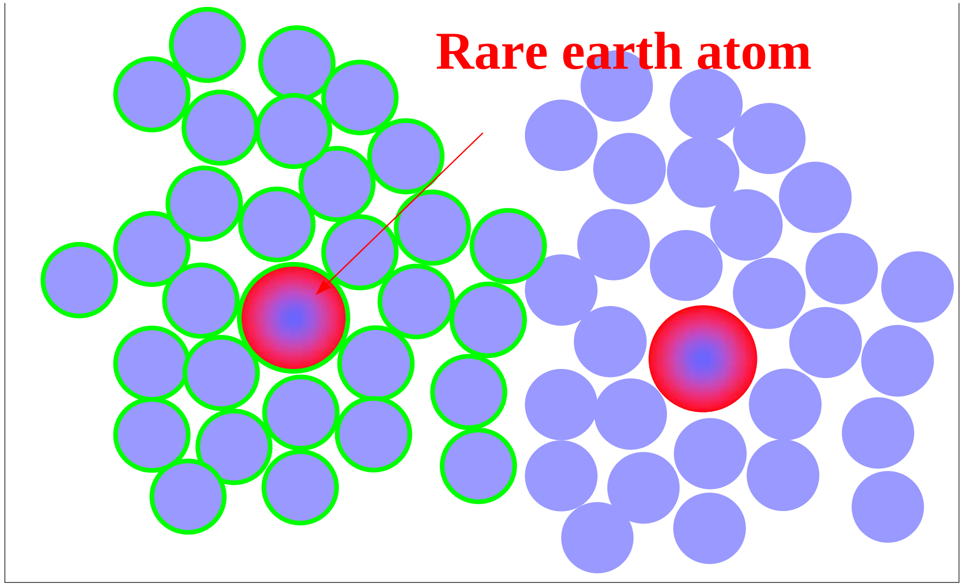


Correlation function Φ(q; t) of liquids at diferent T, solid lines are fit with KWW function.

Diffusion constant of Cu changes due to 1 at% Nb by 75% !



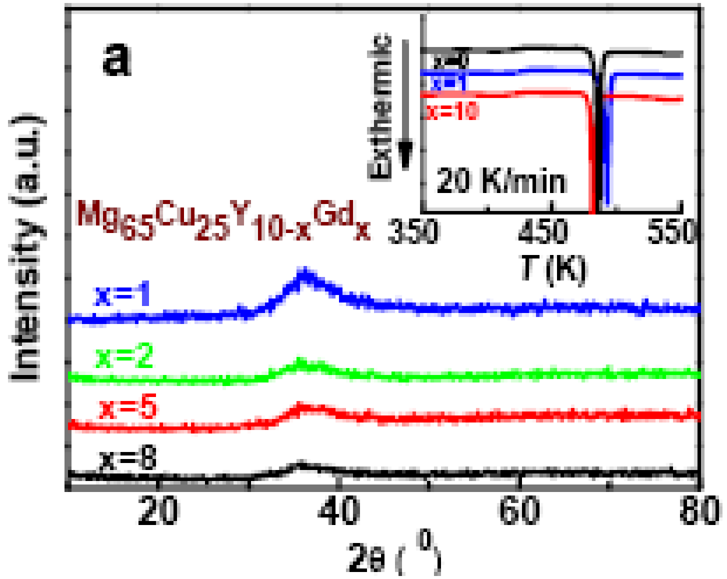
Self-diusion of Cu in the two liquids derived.



Will the Disorder induced localized-itinerant transitions of 4*f* electrons in adding rare earth elements?

Most RE elements have deep localized *f* electrons and Gd has deepest localized *f* electrons and Gd-contained compounds always behave magnetic ordering instead of Kondo effect.

Y has no *f* electron



$Mg_{65}Cu_{25}Y_{10-x}Gd_x$ (x=0, 0.5-10) BMGs

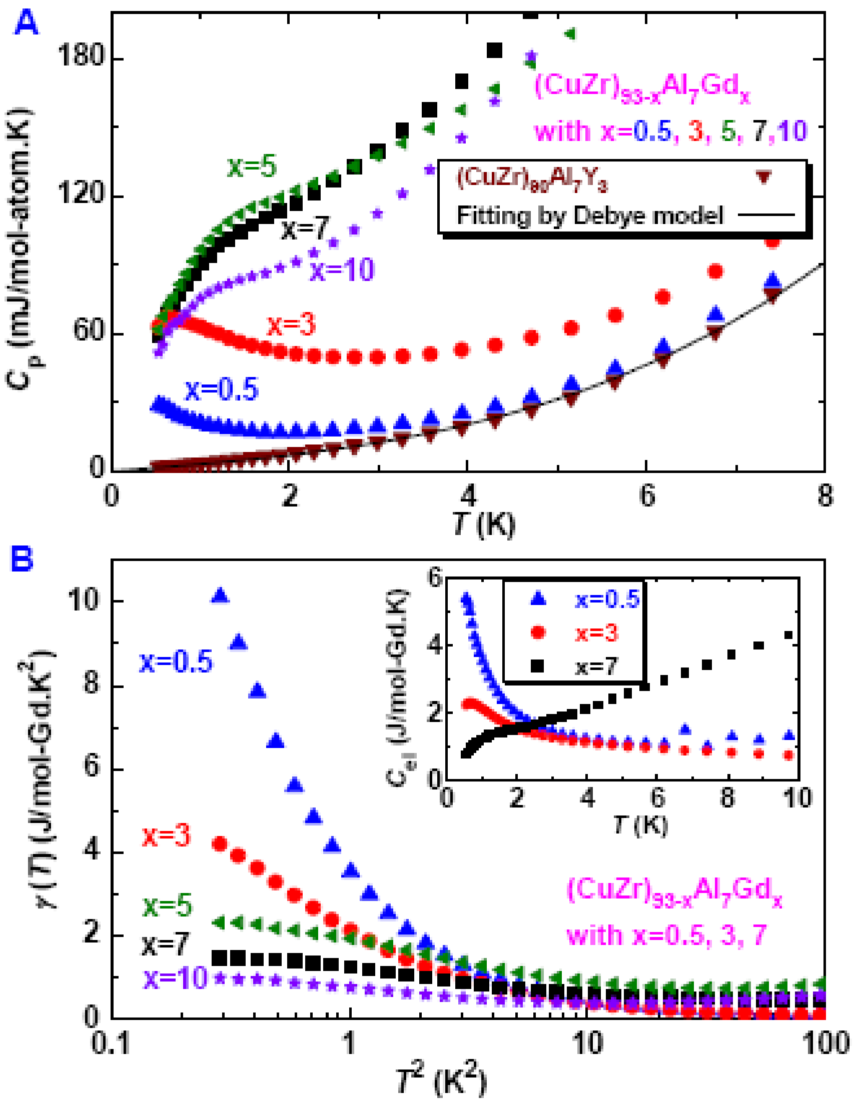
$(CuZr)_{93-x}Al_7Gd_x$ (x=0.5-10) BMGs

$(CuZr)_{93-x}Al_7Y_x$ (x=0.5-10) BMGs

Giant Low-T properties changes by microalloying

$(CuZr)_{93-x}Al_7Gd_x$ (x=0.5, 3, 5, 7, 10) BMGs

$(CuZr)_{93-x}Al_7Y_x$ (x=0.5, 3, 5, 7, 10) BMGs



(A) $C_p(T)$ **vs.** T**. The filled symbols are** Cp **of BMGs with a peak-like deviation from Debye model. The line is fit to** $(CuZr)_{90}Al_7Y_3$ **according to Debye model,** $Cp=\gamma T+\beta T^3$

(B) $\gamma(T)$ $[\gamma(T)=C_{el}/T]$ **vs.** T^2 **of the BMGs.** C_{el} **is gotten by subtracting the data for Y additional BMGs from corresponding Gd-additional BMGs.**

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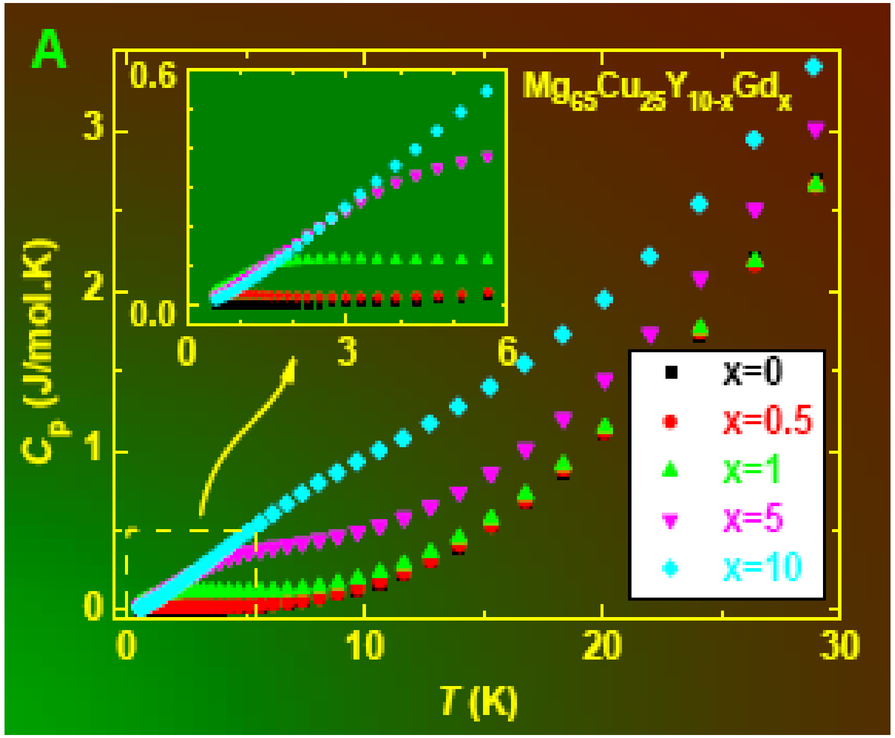
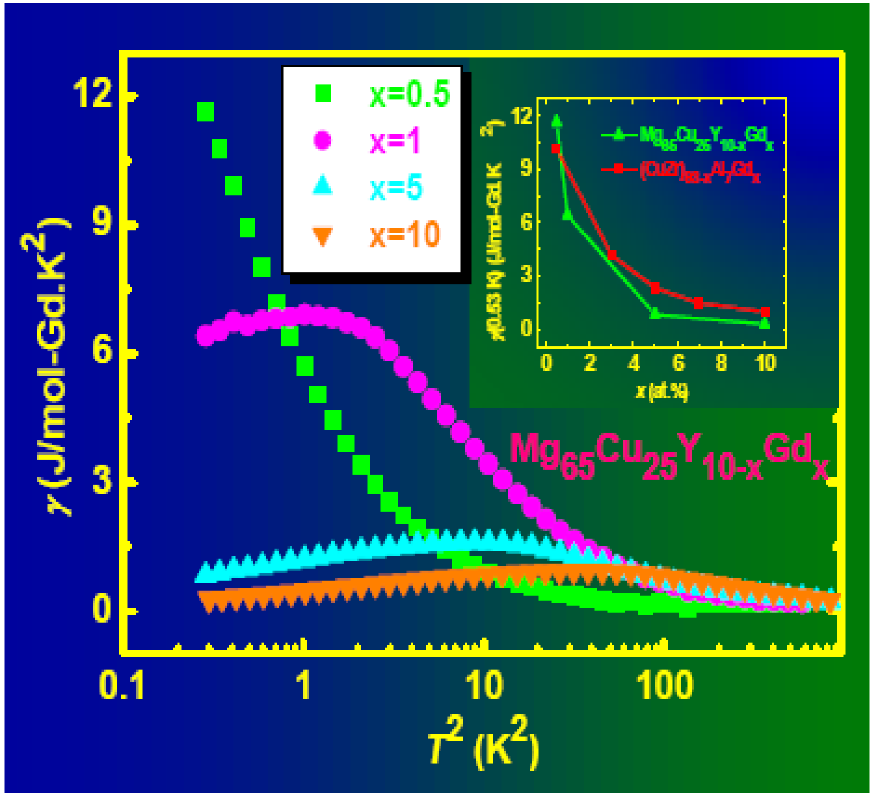
$Mg_{65}Cu_{25}Y_{10-x}Gd_x$ (x= 0.5, 1, 5, 10)

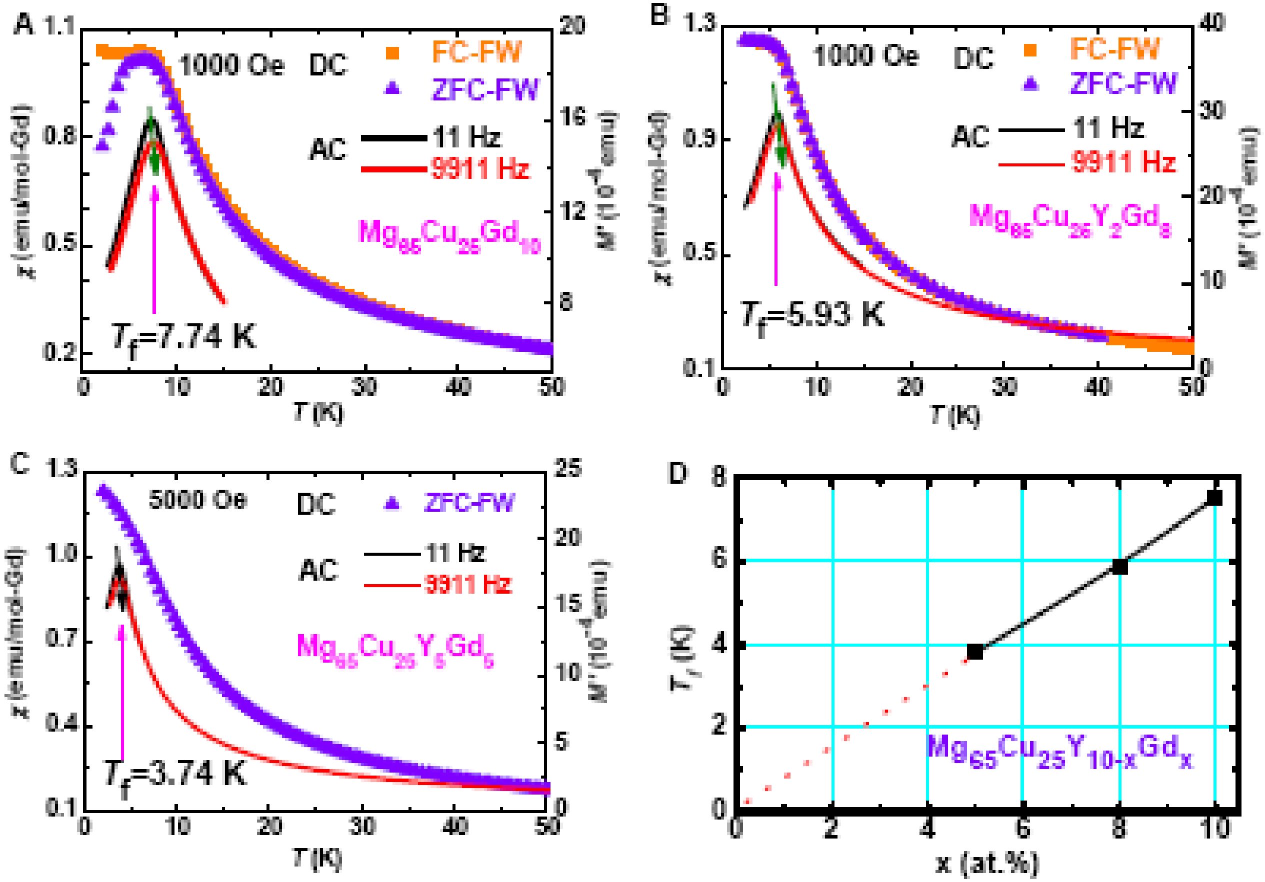
$C_p(T)$ vs. T of BMGs. The $C_p(T)$ of $Mg_{65}Cu_{25}Y_{10}$ was measured as a reference & fitted by Debye model.





$\gamma(T)$ [Cel(T)/T] vs. logarithmic T^2

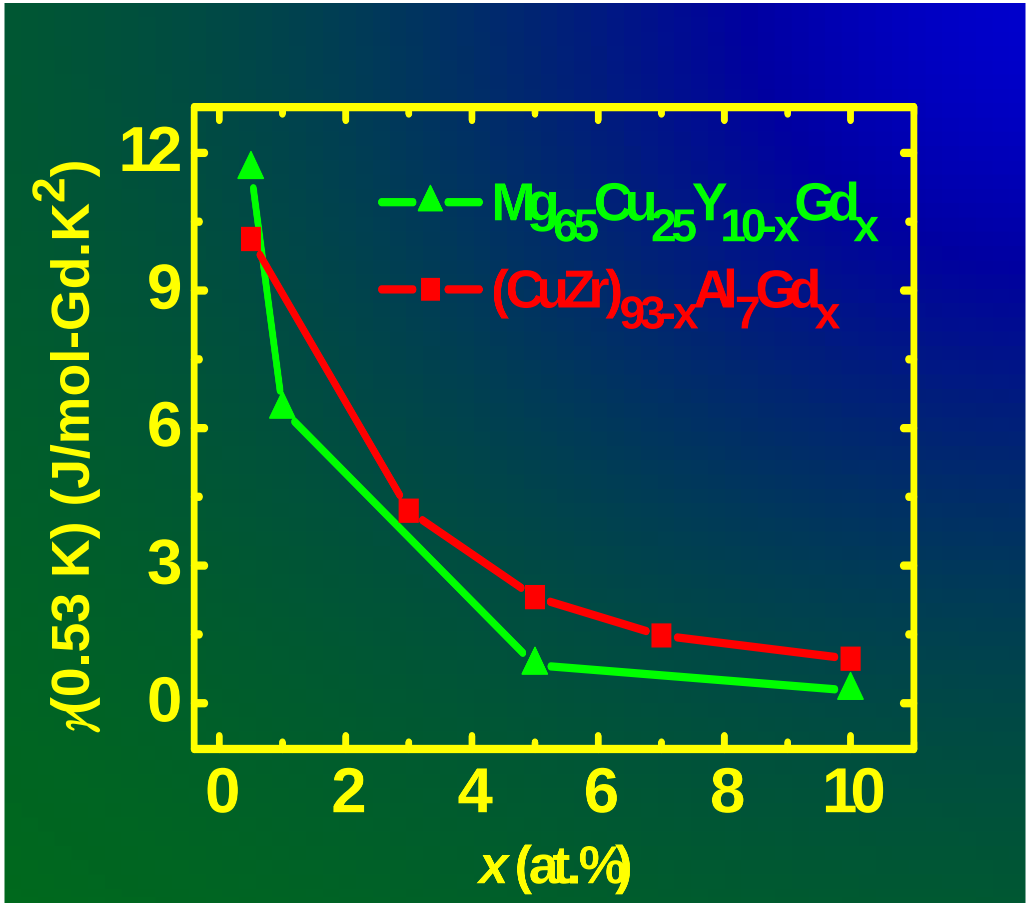
$Mg_{65}Cu_{25}Y_{10\text{-}x}Gd_x$ (x= 5, 10)



(A)- (C) show the *T*-dependent *dc* and *ac* susceptibility for x=10, 8, and 5 samples, which testify the spin glass and inhomogeneous magnetic behavior (D) The black square symbols and line show frozen temperatures of spin glass, T_f, for the previous three samples. The red short dashed line is drawn to show trend of T_f along with concentration of Gd.

$Mg_{65}Cu_{25}Y_{10-x}Gd_x$ (x= 0.5, 1, 5, 10)

$(CuZr)_{93-x}Al_7Gd_x$ (x=0.5, 1, 5, 10)



γ(0.53 K) vs. concentration of Gd. Both of the two Gd-microalloyed systems show that the value for γ goes up quickly along with the decreasing of concentration of Gd.

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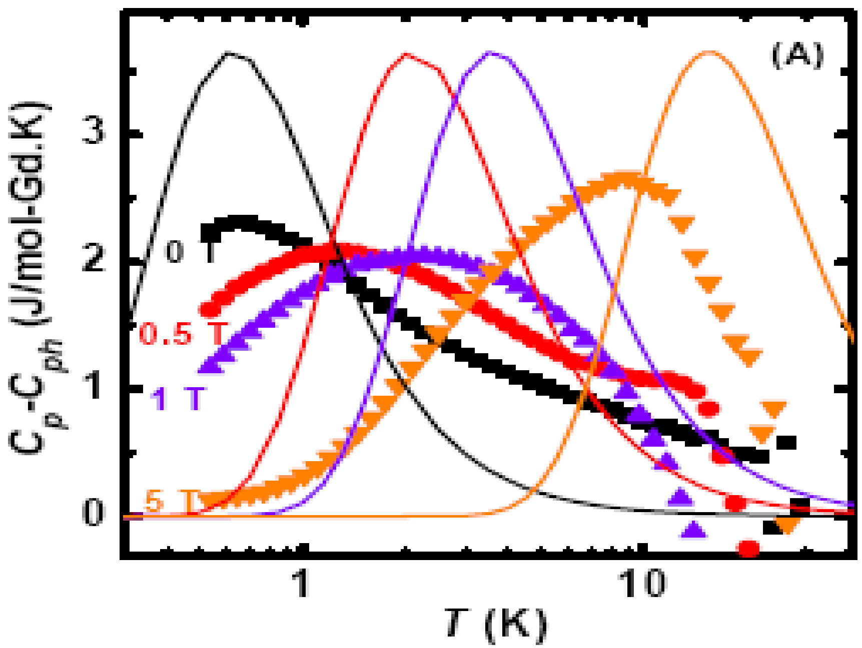
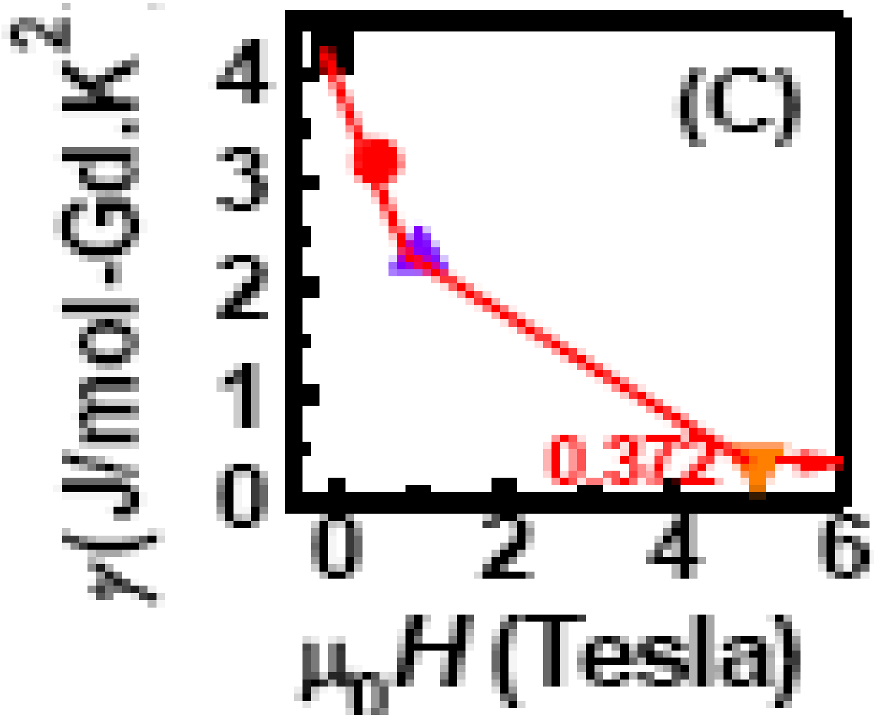
Schottky anomaly?

$(CuZr)_{90}Al_7Gd_3$ BMG





$C_p(T)$ vs. T for BMG under 0, 0.5, 1, and 5 Tesla. The fitting by free-spin Schottky anomaly are shown.

γ(0.53 K) vs. $\mu_0 H$ for, the value for $\mu_0 H$=5 T is still very large.

Schottky type $C_m \sim 1/T^2$

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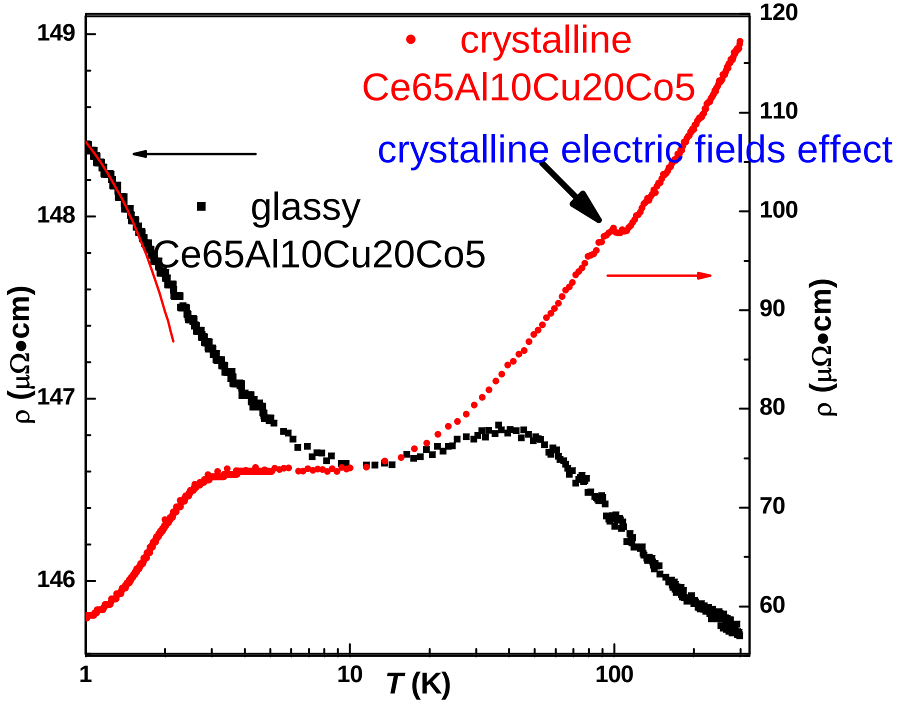
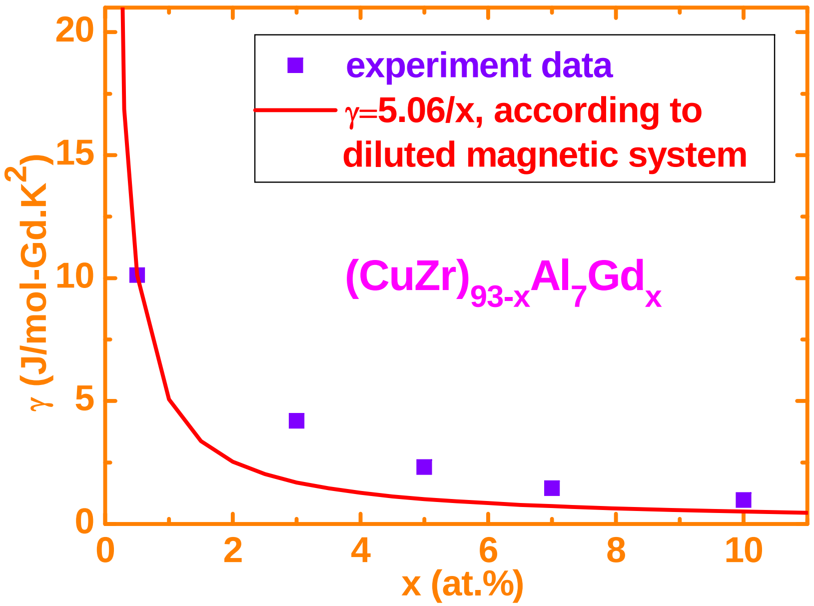
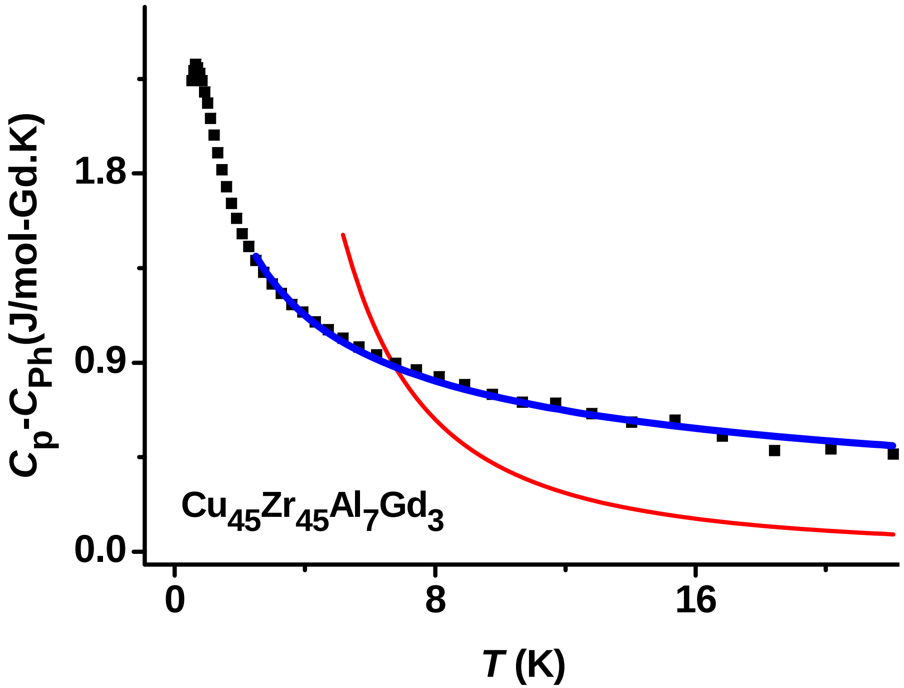
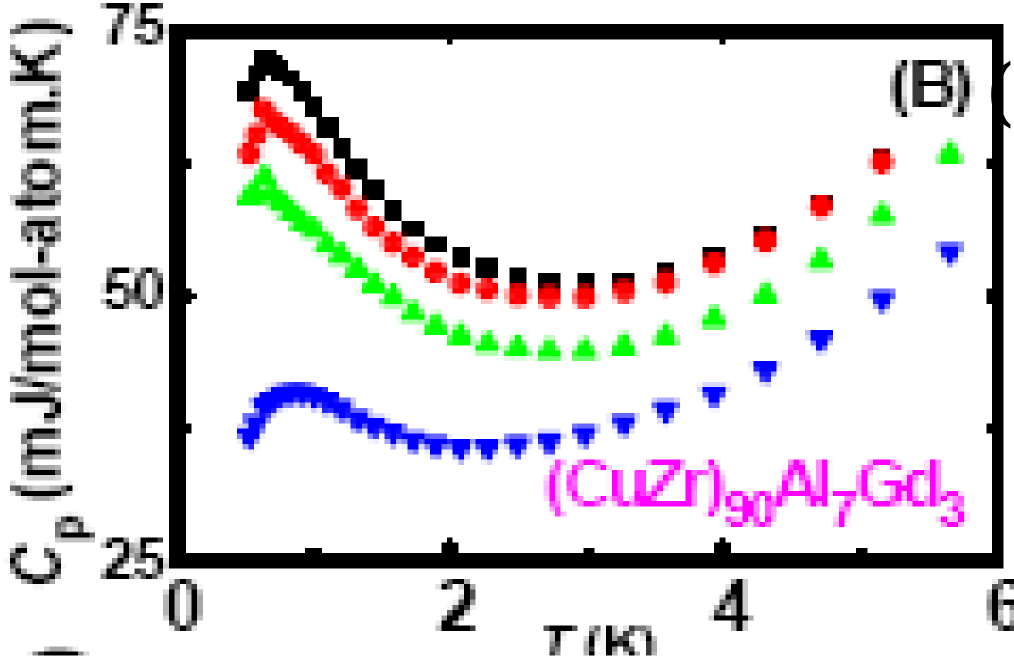


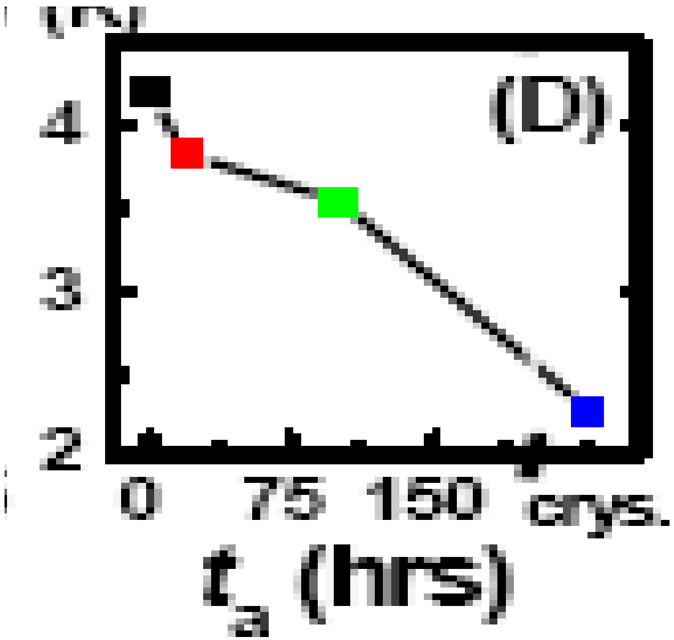
Schottky type $C_m \sim 1/T^2$





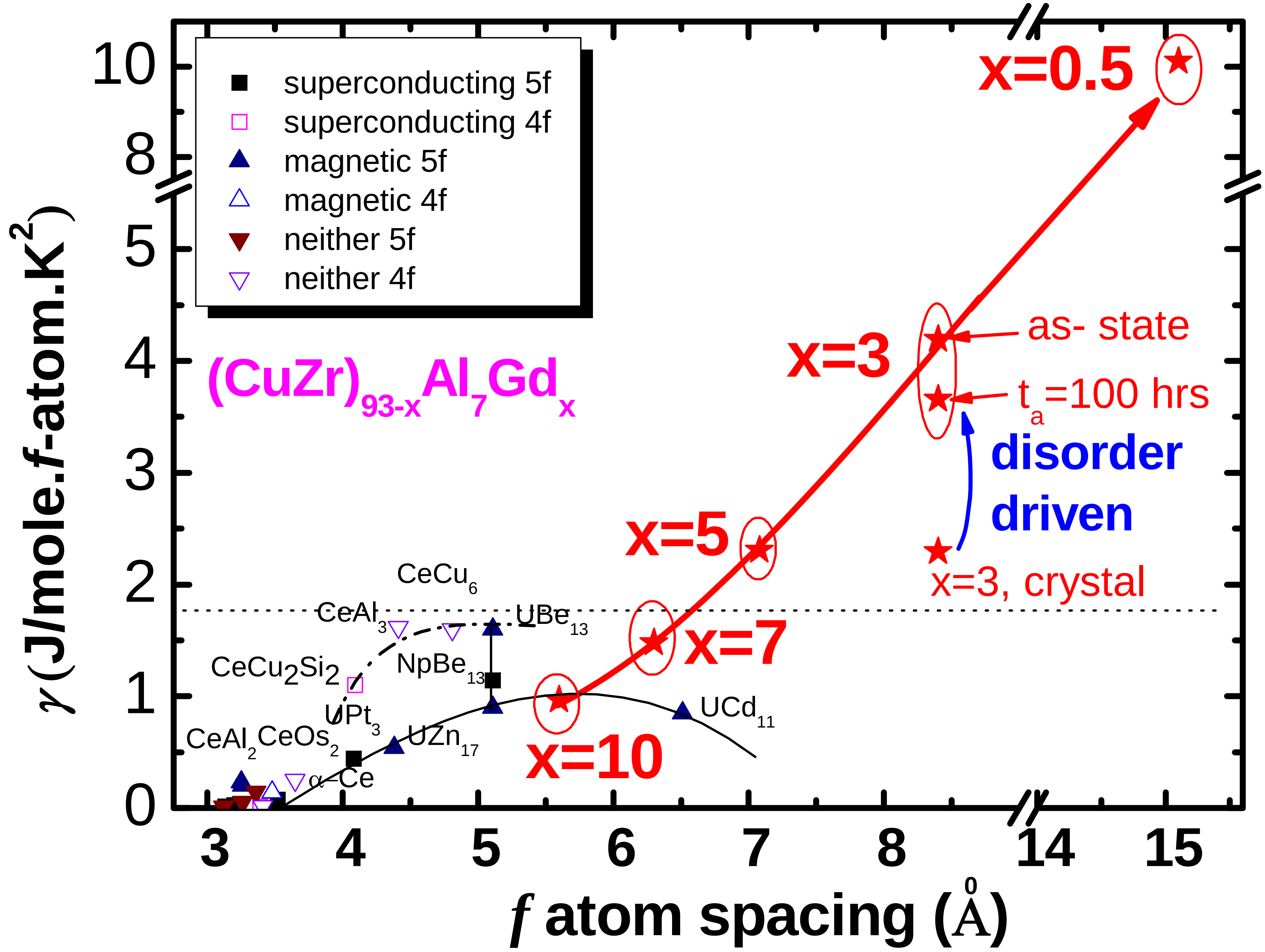
Influence of intrinsic structural Disorder



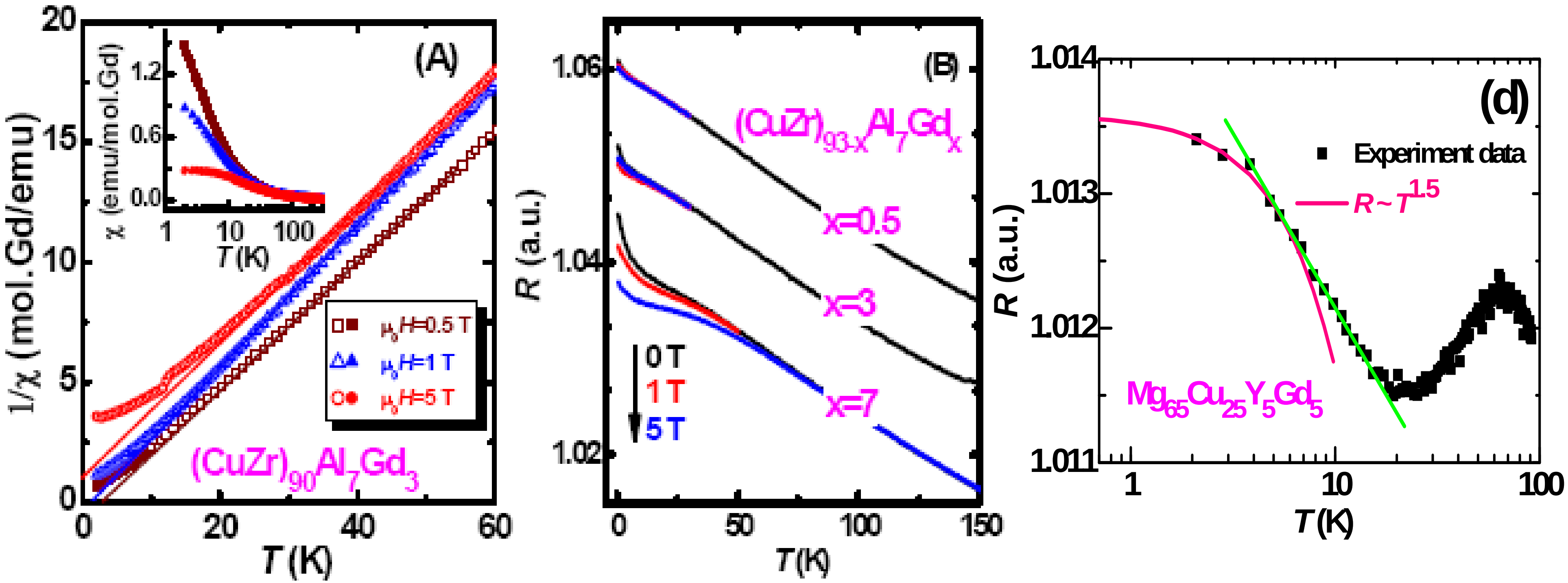


(B) T-dependent C_p of BMG annealed at 0, 20, 100 hrs at 663 K, and crystallized sample. The $C_p(T)$ gets frustrated when annealed, but the peak-temperature and shape do not change obviously until the sample is totally crystallized.

(D) γ(0.53 K) vs. annealing time.



superconducting 5f
superconducting 4f
magnetic 5f
magnetic 4f
neither 5f
neither 4f
(CuZr)93-xAl7Gdx
x=0.5
x=3
as- state
ta =100 hrs
disorder driven
x=3, crystal
x=5
x=7
x=10
CeCu6
CeAl3
UBe13
CeCu2Si2
NpBe13
UPt3
UCd11
CeAl2
CeOs2
UZn17
α-Ce
γ (J/mole.f-atom.K2)
f atom spacing (Å)
0
1
2
3
4
5
8
10
3
4
5
6
7
8
14
15

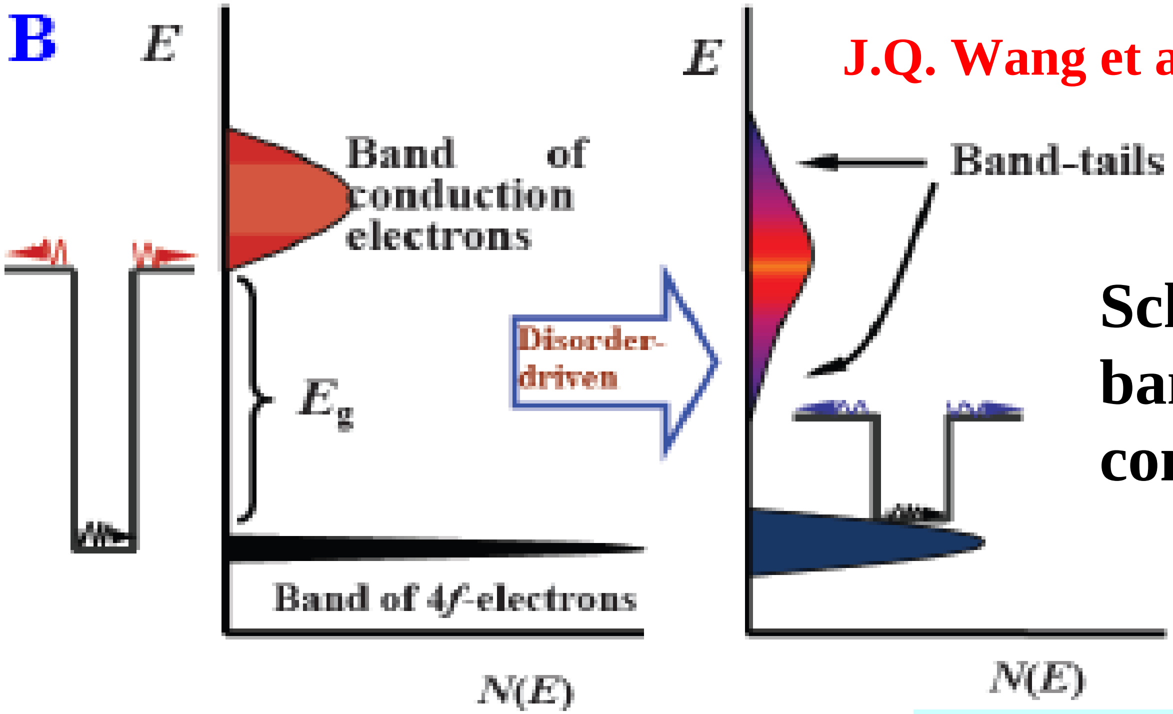


(**A**) ***T*-dependent susceptibility BMG under different magnetic fields. Inset: χ vs ln*T* under H with fitting data** $\chi \sim T^{-1+\lambda}$ **(λ=0.89). The effective magneton** μ_{eff} **of Gd atoms is determined to be 8.04(9)** μB **and is close to the theoretical value**

(B) *T*-dependent resistance under different magnetic fields.
field-driven turn-up behavior at low-*T* is typical Konto behavior.

(c) **Kondo behavior observed in Gd-alloyed BMG. The fitting line of** $R \sim T^{1.5}$ **denoting a NFL behavior**

Possible reasons for Kondo effect in BMG



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Schematic energy band structure of Gd-contained alloys.

Roles of strong structural disorder :

(1) heavy "band-tails" of conduction bands;

(2)broadening of *f* energy band;

(3)The depth of the square-energy-trap decreases

Some localized *f* electrons of Gd are much close to the Fermi energy level and makes the interaction b/n *f* and conduction electrons possible

Summary

1. **We find that HF behavior can occur in strongly Ce-based disordered alloys and important role of disorder in Kondo effect**

2. **Minor addition can induce Kondo effect in BMGs; Microalloying can be used as atomic and electronic "probe" to study atomic and electronic structures in metallic glasses**

3. **The BMGs with strong e-e correlations provide new model system to study and understanding Kondo effect and NFL**