The possibility of nanostructure character in approaching Kondo effect

N Kamali, A Yazdani and L Shahsavari
Tarbiat Modares University, Jalal al Ahmad, P. O. Box14115-175, Tehran, Iran
E-mail: negin kamali6184@yahoo.com

Abstract: Based on instability of magnetic structure, a new class of heavy fermions is constructed with a stable local magnetic ion ‘Gd’. The lattice constants, D.C magnetic susceptibility and the electrical resistivity measurements in the magnetic unstable intermetallic compounds show; (1) the Instability of crystal structure, as well as high transition temperature “\( T_c \)”, strongly depends on the conduction electrons concentration. The reduced size effect and the reduction in correlation length, is expected to be the cause of this behaviour as it could be due to the nanostructure character as well as the competition of inter and intra-cluster also (2) the coexistence of Kondo lattice behaviour and magnetic ordering ‘reentrant antiferromagnet’ for the temperature range of 30<\( T_k <90 \)K with \( T_{N} = T_{max}=30 \)K and finally (3) the metal-insulator-like behaviour with complete quench of magnetic ordering occur antiferromagnetically named “super paramagnet” at a certain conduction electron concentration.

1. Introduction

Even though many of the ground-state properties of elemental Gd, as stable s-state with the electronic configuration of 4f\(^7\) (5p\(^6\) 5s\(^2\) ) 5d\(^1\) 6s\(^2\) and the following characters are well defined experimentally [1, 2, 3], but a numerous experimental and theoretical [2] features of its Intermetallic Compounds, “IMC”,Gd\(_x\)X (X=Al,Au) are still contradictory [4, 5, 6], such as the unusual double magnetic transition, meta-magnetic behavior [7] and their high magnetic moment \( \mu_{eff} =9.6\mu_{B} \) [8]. The Gd element crystallizes in the hcp structure with inter-atomic distance of \( R_{ij}=3.6 \) Å while Gd\(_x\)X is orthorhombic with \( R_{ij}=3.16-3.6\) Å. On the other hand, we are aware that the magnetic character of Gd is F.M with \( T_{c}=\theta_{p}=293 \) K (where \( \theta_{p} \) is the paramagnetic Curie-wise temperatures), the effective magnetic moment “\( \mu_{eff} \)” of 7.6 \( \mu_{B} \) and, the zero temperature moment to be \( \mu_{sat}(T=0) =7.63 \mu_{B} \). These values indicate that the induced polarization of conduction band is at least 0.63 \( \mu_{B} \) which arises from an inter-band exchange coupling (RKKY-type), between the itinerant 5d/6s conduction band electrons and the localized 4f-electrons [9]. Therefore the nature and character of d conduction electrons, c.e, should change and fluctuate in the “s-d” range where the shouldering of f-local-electrons on the d-band is also reported [10]. In order to consider the character of c.e, the exchange correlation energy as well as the exchange fluctuation is investigated on the double phase transition which can be the main cause of; (a) the instability of crystal and magnetic characters, (b) the competition between the RKKY magnetic exchange and the Kondo phenomena and therefore, one of the most interesting points in heavy fermion formation. In this case the energy of ground state depends on the relative magnitude of the RKKY (inter ionic coupling) or the Kondo (on-site coupling) energy. Also in a nano-magnetic system (i.e. where only the Kondo effect dominates) the multi-levels of Kondo energies can be noticed [11] where, the observation of two stages of Kondo energies were reported; The first screening stage
with $T_{K1}$ energy scale is an under-screen Kondo effect which reduces the net spin from 1 to 1/2. In the other ($T_{K2}$) the Kondo effect causes the quench of different spins and makes their value to be $S=0$. Consequently following to our previous works on the observable Kondo lattice behavior of Gd [12] and shape and c.e concentration dependency of magnetism due to strong inter-planar “a-b” exchange which is a cause of distortion [13], the possibility of nano particle formation should be considered.

2. Sample preparation
The initial elements were Gd of 4N purity and Al and Au of 5N. The master sample of Gd$_x$Au$_{1-x}$Al$_{1-x}$ (x=0.4, 0.3) was prepared by melting these elements together in a conventional induction furnace in pure dry argon atmosphere. Annealing was done at 600 °C during 95 hours. And the X-ray patterns proved that our sample was single phase within the accuracy of the method and had crystallized in orthorhombic Pnma space group of Co$_2$Si type structure [13]. By a vibrating sample magnetometer, the DC susceptibility measurements were carried out on the sample in the temperature range of 4.2-300 K while the applied fields were between 100 G to 10000 G.

3. Results and discussions
A key issue of fundamental researches is to understand the effects of structural distortions as well as defects, on extrinsic magnetic properties which are present in every real nanostructure. The following manifested behaviors forced us to suggest the coexistence of Kondo and nano-structured particles where it can still be questioned; Which one is the cause or source of the other? And whether the exchange interaction or distortion is the main cause of these characters, as both are related to the c.e concentration? The exchange interaction, $J_{ij}$ which is a function of the topology of magnetic ions $|R_i - R_j|$, can be calculated as a function of the lattice parameters ($\xi = 5.65$, $\beta = 5.25$, $\gamma = 9.35$ Å), $J_{ij} \propto z^2 F(2Kf |R_i-R_j|)/E_f$ [12] where, $z$ is the ratio of the number of free electron in unit cell. The calculated results of sign and strength of the exchange interaction, $J_{ij}$, show a distortion in the topological structure sites of magnetic ions which is due to the change in inter-atomic space of the closer nearest neighbors - which has the least distance from each other, even than the nearest neighbors - in the range of 3.16 Å $\leq R_c \leq 3.6$ Å (table 1) named “intra-cluster” and is the main cause of the expected behavior.

**Table 1.** Exchange interaction, $J_{ij}$, for the closer nearest neighbours in correlation length of 3.6 Å.

| Gd I | | Gd II |
|------|------|------|
| $R_c$ | $J(R_c-R_i')$ erg$^{-1}$ | $J(R_c-R_i')$ erg$^{-1}$ |
| 3.168 | -7.615 | 1 |
| 3.303 | -4.554 | 2 |
| 3.389 | -4.554 | 2 |

The reduction of correlation length of Gd (from $R_c$=3.6 Å to 3.16 Å) for the 8 closer nearest neighbors with strong exchange interaction, could be the main cause of the formation of intra-cluster interactions (grain size) which could be also the base of isolated nano size formation. The lattice parameters where calculated from the observed X-ray pattern. The results show a considerable enlargement of the unit-cell volume (figure 1), which is mainly affected by the increasing of c.e concentration, in spite of the fact that the ionic radius of $R_{Au}^{3+}$>$R_{Al}^{3+}$. It is evident that the lattice constants drastically depend on the c.e concentration and not on the size effect where the parameter c is rigorously expanded and a and b are contracted and expanded respectively in the direction of; (i) the strong distortion of the “a-b” plane which is due to the strong intra-plan exchange interaction of magnetic ions $J_{in}^{a-b}$ and (ii) the enlargement of c which is caused by the decreasing of exchange between the inter-plans.

Consequently in each point of view the influence of reduction of correlation length on the intra-cluster region due to the strong intra-atomic exchange or the strong exchange interaction in the “a-b” planes (which is the cause of distortion and linear increase of c-direction as well as decreasing of the
inter-planer-exchange), can be the cause of nano crystal formation in cluster. In order to investigate
the nano sized grain, the Debye-Scherrer relation \(d = \frac{0.94 \lambda}{D \cos \theta}\) is applied on the width of lines
with the most intensity in the X-ray patterns (figure 2) where, the size of nano particles is about 20
nm. Needless to state it is an intrinsic property of them and can be affected only by the annealing
process. Based on the reference sample (10 \(\mu\)m), the size of nano-crystalline Gd is reported to be 13
nm [14].

\[ \text{Figure 1. Volume of the unit cell vs. conduction electrons concentration.} \]

\[ \text{Figure 2. The X-ray diffraction for different measuring temperatures (a) 183 K, (b) 100 K} \]

Therefore the measured critical point of “x=0.4” is only one isolated point which positions between
the two mentioned categories. It is interesting to note that we have observed the Kondo behavior only
for this compound \(x=0.4\) while our calculations of RKKY inter-ionic interactions show exactly at
this point the RKKY coupling is at its minimum value [12]. In figure. 3 the variations of susceptibility
vs. temperature for \(x=0.3-0.4\) have been illustrated in different magnetic fields. The measurements
were made with the powdered samples which were warmed up to 300 K in the applied field, after
being cooled down to liquid helium temperature in the absence of field. The cooling in presence of
field and that bellow \(T=100\) K in zero field, are applied to observe the thermal and magnetic history. It
is evident that the Curie temperature is a broad shouldering and the magnetic structure can be
destabilized where, the phase transition is found to be too smeared and a mixture of transitions exists
in low magnetic fields. This critical point of instable magnetic character \(x=0.4\) becomes extremely
sensitive to the physical parameters of the sample (annealing process and the applied magnetic field).

If this point of \(x (=0.3,0.4)\) is closed to the critical value, near the double FM, AFM percolation
threshold due to the competition of inter and intra-cluster, it should be the point at which no frustration
(or competition) occurs, and then the system can stabilize so that \(\Sigma \varepsilon_{ij}J_{ij} = 0\). This takes place at a
certain c.e concentration and applied magnetic field at which the ferromagnetic region is prevented
and the sample behaves paramagnet above the \(T_c=T_N=30\) K. This behavior above 50 K indicates that

\[ \text{Figure 3. Temperature dependence of magnetic susceptibility, for } x = 0.3 \text{ and } x=0.4 \text{ in } H=1000 \text{ G} \]

(a) and for \(x=0.3\) in different magnetic fields (b).
the local magnetic moment has a quantum magnetic number equal to zero (m=0). While the temperature reaches to the $T_K$, we can observe a progressive increase of $\chi(T)$ vs. decrease of temperature. The falling behavior and the prevented F.M-Curie region observed in the $\chi(T)$ curve indicates that, the correlation in RKKY energy is decreasing. This is corresponding to the defined reductions of the cluster size. As it is expected, the weak presence of RKKY follows in a way that: (i) the Kondo effect is shown more effectively [15] and (ii) the more isolated cluster region is due to the reduction in the inter-atomic space from 3.6 Å for pure Gd to 3.16 Å for x=0.4. This anomaly can be attributed to appearing of a virtual bond state which localizes the conduction electrons, and therefore is the beginning of Kondo clouds formation. And the intra-cluster exchange overcomes the inter-cluster and system behaves completely as an isolated clustering region, in this case the resistivity should be high and the Kondo effect should change to complete heavy fermion (figure. 4).

In fact, the interactions between the Kondo clouds (made of localized electrons) and itinerant electrons form a narrow resonance at the Fermi level named “Abrikosov-Suhl” resonance [16]. It can be concluded that the structural distortion is due to the strong intra-cluster exchange in the range of correlation length, 3.16Å <Rc<3.4Å, with 8 more nearest neighbors which can be the cause of isolated nanoparticle formation at a critical concentration of c.e at which; (1)The X-ray diffraction follow the Debye-Scherrer with nano size 20 nm (2) The magnetic phenomena is sensitive to physical parameters where the character of system is changed to the super paramagnetic at which domain wall pining-like can be observed below $T_o= 30K$ (3) The heavy fermion like is the character of inter-cluster exchanges.

Acknowledgements
The authors want to give their special thanks to Dr. S. Neeleshwar for his kind assistance in doing the measurements at the Institute of Physics, Academia Sinica, Taiwan.

References
[1] Wu R, Li C, Freeman A J and Fu C L 1991 Phys.Rev.B 44 9400
[2] Kurz P, Bihlmayer G and Blugel S 2002 J.Phys.Condens.Matter 14 6353
[3] Santos C, Nolting W and Eyert V 2004 Phys.Rev.B 69 214412
[4] Gamari-Seale H and V.Bredimas 1983 J.Magn.Magn.Mater 36 131
[5] Bredimas V, Papatriantafyllou K and Gamari-Seale H 1983 Phys.Stat.Sol b 117 513
[6] Yazdani A and Gamari-Seale H 1986 Phys.Stat.Sol a 96 587
[7] Li X G, Satus M and Takahashi S 2000 J.Magn.Magn.Mater 212 145
[8] Yazdani A 2005 J.of Applied Phys. B 97 113
[9] Kasuya T 1993 JALCOM 192 11-16
[10] Harmon B N and Freeman A J 1974 Phys.Rev.B 10 1979
[11] Sasaki S et al 2000 Nature 405 264
[12] Yazdani A and Khorassani R 2000 Physica B 281 178
[13] Yazdani A and Gardner J S T 1998 Phys.Stat.Sol. (b) 208 465
[14] Krill C E and Birringer R 1998 Philos. Mag. A 77 621
[15] Doniach S 1977 Physica B 91 231
[16] Yu O et al 2002 Nature 415 507