# HOW THE KONDO EFFECT CAN EXIST IN Gd INTERMETALLIC COMPOUNDS

A. Yazdani[1*] and R. Rajaie Khorassani[2]

[1] *Tarbiat Modarres University, Tehran, Islamic Republic of Iran*
[2] *Azad University, Tehran, North Branch, Islamic Republic of Iran*

## Abstract

Based on the crystal and magnetic structural properties of some Gd intermetallic compounds, it is shown that with increasing conduction electron concentration, Gd experiences electronic and magnetic instability, and that these behaviors point to the appearance of Kondo Lattice. We suggest that the conduction electrons have gained local character. It is shown that Kondo effect should be observed at around x=0.4. Resistivity studies confirm the calculations, and a Kondo temperature of around 70 K found for $Gd_2Au_{0.4}Al_{0.6}$.

## Introduction

The theory of magnetic moment formation in intermetallic compounds has been a controversial subject for many decades [1,2]. One of the major places of dispute has been whether a model based on localized or itinerant electrons is the most appropriate or rather which of the concepts of electron fluctuation, hybridization or electron localization are dominant.

We considered how magnetic instability in itinerant intermetallic systems arises. We chose as the subject of our study rare earth magnets with very stable 4 f electrons, in particular Gd, with the aim of investigating the possibility of the Kondo effect (Kondo Lattice) in $Gd_2Au_xAl_{1-x}$ intermetallic compounds.

Investigation of the magnetic and crystal structural behavior of $Gd_2Au_xAl_{1-x}$ reveals a dependence of these properties to the behavior of free electrons. The variation of magnetic susceptibility with temperature for $Gd_2Al$ and its magnetic heat treatment shows magnetically unstable phase transition [3].

**Keywords:** Kondo Lattice; Electrin localization

* *E-mail:yazdani@modares.ac.ir*

In contrast to $Gd_2Al$, $Gd_2Au$ shows much more stable magnetic phases and no magnetic viscosity [4]. X-ray data shows that $Gd_2Au_xAl_{1-x}$ $(0 < x < 1)$ remains orthorhombic throughout this range, with 8 magnetic Gd ions in two nonequivalent positions [5,6]. The only difference being the conduction electron concentration (CEC), with an increase in x as $Au^{+1}$ is substituted by $Al^{+3}$, ($Gd_2Al$, $Gd_2Au$) and therefore CEC, Spin density reduces and no gelation effect is seen.

## Experimental Results and Modeling

Investigation of the magnetic and structural behavior of $Gd_2Au_xAl_{1-x}$ compounds reveals the following observation which shows a dependence of crystal structure and magnetic structure and instability on conduction-electron concentration (CEC).

1. X-ray studies of the lattice parameters (Fig. 1) show a nonlinear dependence on CEC(x) and a deviation from Vegard's rule:

$$\begin{aligned} a(x) &= 6.526 - 0.264x + 2.409x^2 - 1.591x^3 \\ b(x) &= 5.370 + 0.504x - 2.997x^2 + 2.072x^3 \\ c(x) &= 9.489 - 0.043 - 1.173x^2 + 0.736x^3 \end{aligned} \quad (1)$$

2. The variation of magnetic susceptibility with

temperature for x=0.2, x=0.4 and x=0.6 compounds shows a difference between needle (n) and powder (p) sample forms [7] (Fig. 2).

Having equivalent lattices, this difference in magnetic susceptibility between powder (p) and needle (n) forms must be related to interactions involving conduction electrons.

The shape dependence of magnetic behavior (Fig. 2) and the gap between the powder and needle samples at x=0.2-x=0.6 (in the same range where the deviation from Vegard rule is exhibited) reveal existence of a hidden magnetic energy [7]. A low value of X(T) accompanied by a spreading in the magnetic phase transition (not a sharp transition) is also exhibited at x=0.4 (Fig. 2). With increase in CEC, the gap increases too. The above shows magnetic moment fluctuation and great exchange dispersion wfhich make the alignment of the moments not possible.

These behaviors along with a low value of effective magnetic moment ($\mu_{eff}$=4.7 $\mu_\beta$) may be due to a canted system or absorbing electrons that reduce the ferromagnetic moment. The latter can even result in moment compensation. However, in the case of $Gd_2Al$-Au compounds the absorption of electrons is not possible as Al and Gd atoms have filled electron shells, and for Au it is not observable in $Y_2Au$ [8].

These observations point to the conduction electrons becoming bound. Therefore we were led to the idea of the conduction electrons interfering in the magnetic behavior and the occurrence of the Kondo Lattice for $Gd_2Au_xAl_{1-x}$ compounds.

Resistivity studies confirm our line of thought and showed the Kondo effect for $Gd_2Au_{0.4}Al_{0.6}$ (Fig. 3).

We believe ferromagnetic conduction electron polarization forms a ferromagnetic electron cloud around the Gd ion, and that the conduction electrons gain energy due to this spin polarization (RKKY) [9]. Due to the Pauli exclusion principle, the electrons have a spin flip and the polarization acquires antiferromagnetic nature.

## Method of Calculations and Discussion

The first aim of our calculations was to anticipate the x at which the Kondo effect should manifest (for what compound should this effect be observed?). We also wished to calculate the effective mass of the conduction electrons in that compound, which is an important parameter in addition to non Vegard rule behavior showing the extent of electron localization in heavy fermion study.

1. Because of the competition between interionic RKKY [10] regime and the Kondo effect we expect the Kondo effect to show itself where the exchange interaction $J_{ij}$ is at a minimum (as a function of x). $J_{ij}$ is

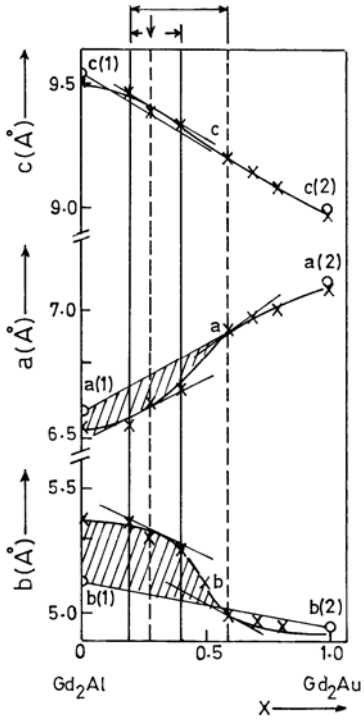


**Figure 1.** Variation of the lattice parameters with x.

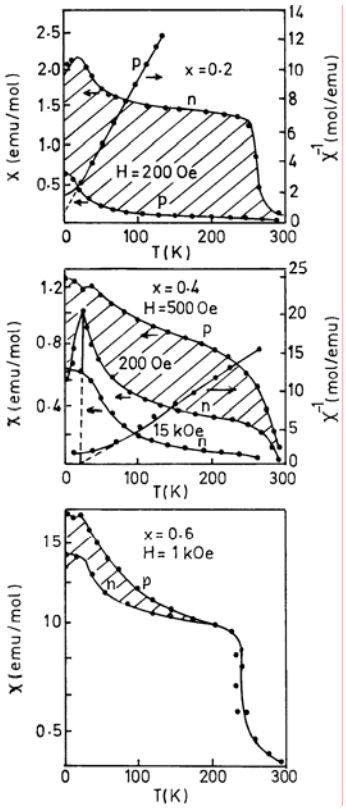


**Figure 2.** Temperature dependence of the susceptibility for x=0.2, 0.4, 0.6, for powder (p) and needle (n) sample in different magnetic field H'.

a function of the topological magnetic ion $|R_i - R_j|$ (interionic distance) which itself can be calculated as a function of the lattice parameters (Fig. 4) and through them as a function of CEC(x), (Equation 1).

$$J_{ij} \propto \frac{z^2 F(2Kf|R_i - R_j|)}{Ef} \quad (2)$$

where

$$F(\omega) = \frac{1}{\omega^4}(\omega\cos\omega - \sin\omega) \quad (3)$$

with $\omega = 2K_f(|R_i - R_j|)$

$K_f$ is the wave number of the electron at the fermi level, which can be evaluated through

$$K_f = \frac{(3\hbar^2 n)^{1/3}}{V}$$

Where V is the unit cell volume evaluated from the lattice parameters and n is the number of free electrons in the unitcell

$$V = |a(x).b(x)\times c(x)|$$

$E_f$ is the energy of the fermi level

$$E_f = \frac{\hbar^2 k_f}{2m^*} \quad (6)$$

Where $m^*$ is the effective mass of the CE.

$$z = \frac{n(x)}{N} \quad (7)$$

z is the ratio of the number of free electrons in the unitcell (n) to the number of magnetic ions in the unitcell (N). Since Gd and Al each donate 3 electrons and Au donates 1 electron to the unitcell, n = 4(9-2x).

GdI has 5 and GdII has 6 nearest neighbors (Fig. 4). $R_i$-$R_j$ has been calculated for these nearest neighbor ion pairs [11] (Table 1). Using the above relations we considered the different ion pairs, and calculated the x corresponding to the minimum $J_{ij}$ for each pair (Table 2). For different ion pairs the minimum $J_{ij}$ occurs at different x. The range of x being between 0 and 1, those values of x which are out of this range are physically unacceptable (x = 0 for $Gd_2Al$ and x = 1 for $Gd_2Au$, no compound with x > 1). Furthermore, X-ray studies show that only the ionic sites of GdII ions show a dependence on x (Table 3), therefore the exchange interactions which have led to magnetic instability and distortions in the lattice parameters must be mainly dominated by GdII ions. The only pair constituted from two GdII ions ($R_{GdII}$-$R_5$) shows a minimum for $J_{ij}$ at x = 0.46 (Figure 5 shows the variation of $J_{ij}$ with x for $R_{GdII}$-$R_5$ and the minimum is seen at x = 0.46). Thereby, we expect the Kondo effect at around x = 0.46, which was confirmed by our experimental work (Fig. 3).

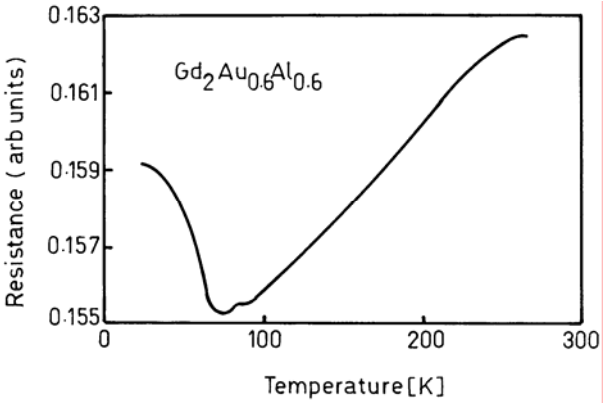


**Figure 3.** Variation of Resistivity with T for $Gd_2Au_{0.4}Al_{0.6}$.

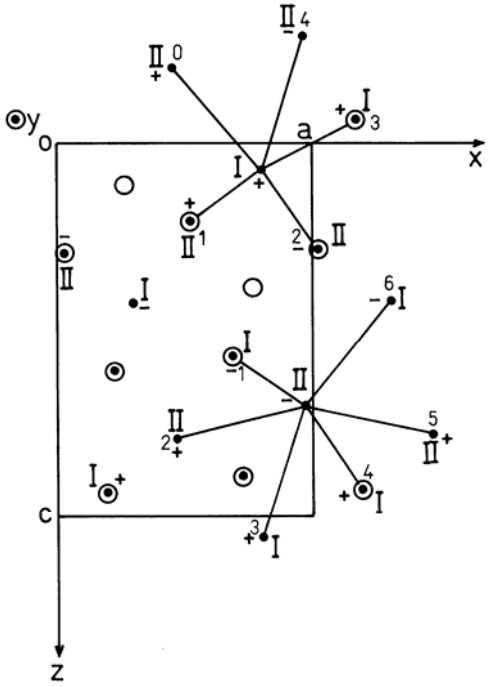


**Figure 4.** Nearest neighbors of GdI and GdII.

2. One of the parameters which can show a measure of electron localization is the effective mass. The more localized the electrons, the heavier their effective mass. Based on the above calculations and experimental results we were led to calculate the electron effective mass for $Gd_2Au_{0.4}Al_{0.6}$ (x = 0.4) and put to discussion

the binding energy and local character of the conduction electrons.

Our experimental results (Fig. 3) show the observed Kondo temperature for $Gd_2Au_{0.4}Al_{0.6}$ to be around 70 K. From the observed Kondo temperature ($T_k$) J(0), the exchange integral between the conduction electrons and the localized 4 f orbital electrons, can be calculated as:

$$T_k = \frac{E_f}{K}\exp(\frac{1}{g(E_f)J(0)} \tag{8}$$

J(0) can also be calculated by

$$J(0) = \frac{2V_m^2}{E_f - E_{4f}} \tag{9}$$

Where $V_m$ is the mixing potential, $E_{4f}$ is the energy of the 4f orbital electrons and $E_f$ is the energy of the fermi level. $m^*$ enters the above relations through $E_f$. By varying $m^*$ in the above relations until the two Js equal, we were able to calculate the effective mass. In $Gd_2Au_{0.4}Al_{0.6}$ we expect $g(E_f)$ to be greater then for pure Gd. Localization of conduction electrons increases the density of states at the fermi level (Fig. 6) (moreover the addition of Au or Al to the Gd lattice increases the entropy and therefore the density of states).

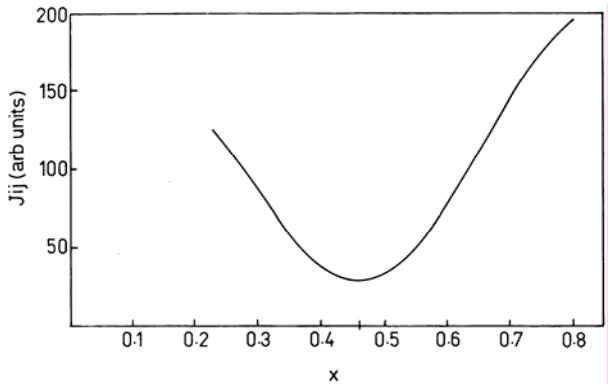


**Figure 5.** Variation of $J_{ij}$ with x.

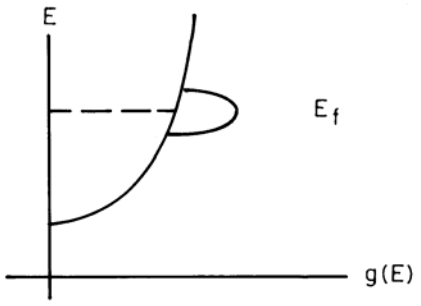


**Figure 6.** Increase of density of states at fermi level due to electron localization.

**Table 1.** $R_i$-$R_j$ for GdI, GdII and their nearest neighbors where X=-0.473x+0.96 and Z=0.067x+0.75

| Gd | Nearest neighbor | $R_i - R_j$ |
|---|---|---|
| GdII | 1 | $((X-0.66)^2a^2+0.25b^2+(Z-0.57)^2c^2)^{1/2}$ |
| | 2 | $(0.25a^2+(2Z-0.5)^2c^2)^{1/2}$ |
| | 3 | $((X-0.84)^2a^2+(Z-1.07)^2c^2)^{1/2}$ |
| | 4 | $((X-1.16)^2a^2+0.25b^2+(z-0.07)^2c^2)^{1/2}$ |
| | 5 | $(2.25a^2+(2Z-0.5)^2c^2)^{1/2}$ * |
| | 6 | $((X-1.34)^2a^2+(Z-0.34)^2c^2)^{1/2}$ |
| GdI | 1 | $((X-0.66)^2a^2+0.25b^2+(0.34-Z)^2c^2)^{1/2}$ |
| | 2 | $((X-1.16)^2a^2+0.25b^2+(0.07-Z)^2c^2)^{1/2}$ |
| | 3 | $(0.109a^2+0.25b^2+c^2)^{1/2}$ |
| | 4 | $((0.84-X)^2a^2+(0.07-Z)^2c^2)^{1/2}$ |
| | 5 | $((1.34X)^2a^2+(Z-0.43)^2c^2)^{1/2}$ |

* This ion pair gave the minimum in $J_{ij}$ corresponding to $x_{min}$=0.46 (Fig. 6)

**Table 2.** The values of $x_{min}$ for the nearest neighbor ion pairs

| Type of Gd ions | $R_j - R_i$ | $x_{min}$ |
|---|---|---|
| II – I | $R_{GdII} - R_1$ | 0.55 |
| II – II | $R_{GdII} - R_2$ | 1.57 |
| II – I | $R_{GdII} - R_3$ | 0.90 |
| II – I | $R_{GdII} - R_4$ | 0.37 |
| II – II | $R_{GdII} - R_5$ | 0.46 * |
| II – I | $R_{GdII} - R_6$ | 1.27 |
| I – II | $R_{GdI} - R_1$ | 1.76 |
| I – II | $R_{GdI} - R_2$ | 0.37 |
| I – I | $R_{GdI} - R_3$ | 0.5 |
| I – II | $R_{GdI} - R_4$ | 1.42 |
| I – II | $R_{GdI} - R_5$ | 1.27 |

* The acceptable value for $x_{min}$

**Table 3.** Structural sites of GdI and GdII

| Compound | Type of Gd | X | Y | Z |
|---|---|---|---|---|
| $Gd_2Al$ | Gd(I) | 0.83 | 0.25 | 0.07 |
| | Gd(II) | 0.96 | 0.25 | 0.075 |
| $Gd_2Au$ | Gd(I) | 0.845 | 0.25 | 0.0671 |
| | Gd(II) | 0.478 | 0.25 | 0.817 |
| $Gd_2Au_xAl_{1-x}$ | Gd(I) | ≈ 0.84 | 0.25 | ≈ 0.07 |
| | Gd(II) | -0.473x+0.96 | 0.25 | 0.067x+0.75 |

Therefore, we considered an arbitrary value of 2.85 for $g(E_f)$ which is greater than the value for pure Gd(1.85) [12]. For $m^*$=29m-35m the J for the two relations coincided.

The large effective mass signifies that the conduction electrons have indeed become bound. With the increase in conduction electron concentration, spin polarization of conduction electrons intensifies, taking the free electrons toward localization.

The unexpected manifestation of the Kondo effect confirms that spin polarization interactions has provided the energy needed for the electrons to spin flip (Pauli exclusion principle) and form an antiferromagnetic cloud, making the Kondo effect possible for the compound x = 0.4 where $J_{ij}$ is at a minimum.

## Appendix

In our calculations, the value of $V_m$ (mixing potential) for $Gd_2Au_{0.4}Al_{0.6}$ was needed. The different values of J(0) reported for Gd compounds lie between 0.04 eV and 0.15 eV [13,14,15]. For $Gd_2Au$(x=1) with the least CEC we considered J = 0.04 eV and $m^* = 3m$. Using equations 6 and 9, $V_m$ was calculated. For $Gd_2Al$(x=0) with the most CEC, we set J = 0.15 eV and considered different values for $m^*$, and obtained the corresponding mixing potential. Considering the variation of V from x = 0 to x = 1 as linear, we were able to calculate a value for the mixing potential of $Gd_2Au_{0.4}Al_{0.6}$ and there upon obtain the result $m^*$=29m-35m.

## References


1. Martin, R. M. *Phys. Rev. Lett.,* **48**, 362, (1982).
2. Brugger, T. *et al., Ibid.,* **74**, 248, (1993).
3. Yazdani, A. *JMMM,* **90&91**, 563-64, (1990).
4. Gammari-Seale H. and Bredimas, V. *Ibid.,* **36**, 131-35, (1983).
5. Pearson, W. P. The Crystal Chemistry and Physics of Metal Alloys, Pergamon Press, p. 532, (1972).
6. Boshow, K. H. J. and Vandergood, A. S. *Journal of Less Common Metals,* **24**, 17, (1971).
7. Yazdani, A. and Gardner, J. St. *Phys. Stat. Sol. (b),* **208**, 465, (1998).
8. Yakinthos, J. K., Ikonomou, P. F. and Anthanotopolos, T. *J.MMM,* **8**, 308, (1978).
9. Fisk, Z., Ott, H. R., Rice, T. M. and Smith, J. L. *Nature*, **320**, 124, (1986).
10. Kasuya, T. *Theor. Phys.,* **115**, 45, (1978).
11. Bredimas, V., Papatriantafillou, C. and Gammari-Seale, H. *Phys. Stat. Sol. (b),* **117**, 513, (1983).
12. Yazdani, A. and Ramazani, A. *J. Sci. Iran,* **9**(3), 273, (1998).
13. Siepler, D. and Elscher, B. *Physica (Utrech T),* **86188 B**, 97, (1978).
14. Lohneysen, H. V., Tholence, J. L. and Steglich, F. Z. *Phys.,* **B29**, 319, (1978).
15. Lieke, W., Moeser, J. H., Steglich, F. *Physik,* **B30**, 155, (1978).