Possibility of HF-formation on Gd-Bi-IMC

A. Yazdani\textsuperscript{a}, S. Nabavi\textsuperscript{b}

\textsuperscript{a}Basic Sciences dept, Tarbiat Modares University, Jalal al Ahmad Exp, P.O. Box 14115-175
Tehran, Iran

\textsuperscript{b}K.N.T University, Tehran, Iran

yazdani@modares.ac.ir

Abstract. Since in the isostructural compounds of Gd4Bi3 and Gd4Sb3 the only parameters which determine the magnetic behaviour as the sign and strength of the exchange parameter, Jij, depend on the following parameters (related to the chemical pressure due to the size effect of RBi>RSb); (1) the topological positions of the magnetic ions, and (2) the nature and the density of the conduction electrons, both of which are strongly depend not only on the nearest neighbor but also on the correlation length defined by the Rc=2kfRij. The Gd4Bi3 should be the critical composite for which Rc is not its extremum value. At this compound, the dominance of dispersion of exchange or even the competition of magnetic ions (intracluster exchange) overcomes the thermal fluctuations \( \mu_R / \mu_0 \approx R_{ij} \) where \( R_{ij} \ll 2 J_{ij} \). This behavior can be the cause of \( T_c = 347 \) K and its drop to 266 K for Gd4Sb3 and even to 110 K with the change of crystal structure for Gd5Bi3, which means that the internal magnetic energy can change to thermal \( (\Delta T_c = 347 - 110 \) K) for the second one).

1. Introduction

Even though the Gd\textsuperscript{3+} is on its stable s-state with electronic configuration and no orbital moment, no crystal field effect and even no direct exchange interactions, as 4f-electrons, lie inside the 5s, 5p closed shell to be screened by them, but among some Gd-nonmagnetic
metals intermetallic compounds the anomalous physical properties and the variety of magnetic characteristics with low carrier is a puzzle [1]. Some various complicated physical phenomena, such as the dense Kondo behavior, the heavy-fermion states, magnetic ordinary and the magnetic polaron effect have been observed and reported in the RX systems [2]. Since indirect magnetic exchange interaction is considered to have the most important effect on physical properties of rare-earth compounds and there is not any other interaction in Gd-IMCs, the configuration of conduction electrons “c.e” ([5d 6s2]) which is strongly influenced by the electronic structure, should be determined.

The character and the nature of c.e are depending on the overlapping of the valence and conduction bands. This overlap is itself a functional of fluctuation regions of “s-d”, defined by $\Delta E_{c-d}$ [3]. This can be referred as d-character that depends on the density of state of conduction electrons, which can even change or stabilized the crystal structure.

Consequently because of the strength of exchange interaction, the nature of c.e could be of d-like or even of the 5d-state [4]. The 5d-state is believed to be band-like which takes part in chemical bonding and thus could be the main source of:

i) The excess (or even reduction) of effective magnetic moment in some Gd-compounds.

ii) The variety of crystal structure and the heat formation can be study through the energy difference of $\Delta E_{s-d}$ where the population is itself a functional of fluctuation of the electrons in the valence and conduction bands, named “inter-band mixing”.

Therefore the crystal structure and magnetic character of GdxBiy should be found out carefully.

Sample preparation and experiment

The samples were prepared from the stoichiometric amounts of the elements (Gd; 99.9, Bi; 99.99) by melting under pure argon atmosphere in an arc-melt furnace with some difficulties. The
samples were re-melted for four times, and heat treated in an evacuate quartz tube below the eutectic temperature.

Since preparing a high quality single crystal of Gd\textsubscript{x}Bi\textsubscript{y} is difficult due to the high vapor pressure, the ampere of arc-melt was selected in the range of 50-150.

The reduction of samples weight before and after the heat treatment was negligible.

X-ray powder diffraction of the sample was examined by Philips X-ray. The spectral lines were examined with respect to the number, position, broadening and their intensities.

The identification of the phase and its lattice constants were determined by a least square program.

The A.C magnetic susceptibility and electrical resistivity measurements were carried out by the standard induction method in a closed refrigerator down to 10K.

### Results and discussion

In spite of the richness of available experimental data on various complicated physical phenomena of Gd\textsubscript{x}Bi\textsubscript{y} "$x/y \geq 1$" [5], the intrinsic electronic structure and mechanism of interchanging of conductivity (as crystal structure and electrical resistivity) and magnetic character are still undefined. Even more the narrowing of compositional range of formation of the IMC "$x \geq 1$" on the phase diagram and the reported peritectic reactions of the Gd\textsubscript{4}Bi\textsubscript{3}, Gd\textsubscript{5}Bi\textsubscript{3} are still not well defined [6].

In this article this systematic consideration is completed and followed by eutectic formation of Gd\textsubscript{2}Bi, which has not been reported yet. Fig.1 (a) shows the variation of heat formation for different compounds "$x/y \geq 1$". It is evident that the heat formation drastically depends on the concentration of magnetic ions, in a way that decreases with the increasing in the number of magnetic ions. This character sensitively depends on the inter-atomic space as well as $k_\text{f}$ (fig.1 (b)), and affects the pair potential and other related factors[7] as well as cohesive energy which is governed by the character and density of conduction electrons.

However since the heat formation and therefore the energy of crystal structure both are related to cohesive energy, it can be suggested that the strong induced polarization of conduction band, which is
interchangeable by $j_{ij} \propto F(k_i(R_i-R_j))$ named “inter-band mixing”, is the main cause of the existing unagreement between electrical resistivity and magnetizem (fig. 1 (c)). Where the heat formation and the magnetic character called "indirect exchange interaction" are considerable through:

1. The energy difference of $\Delta E_{s-d}$ where the characteristic of "c.e" could be s or d-like and,
2. The population of the fluctuating electrons in the valence and conduction band, named inter band mixing which can stabilize the structure.

In each case, the narrowing of the conduction band close to the Fermi level, rather than simply the number of conduction electrons which is a basic parameter in the R.K.K.Y, is suggested to be the main cause.

This suggestion on the other hand can be studied through the temperature dependence of electrical resistivity (Fig.2(a)).

Fig.2 (a) shows:

1) A dramatic change in the electrical resistivity between the Gd$_4$Bi$_3$ and Gd$_5$Bi$_3$ happens where;
   a) It is expected with a higher magnetic momentum by $\Delta \mu_{\text{eff}}$ (Gd$_5$Bi$_3$)=(8.43-7.36) that the low density of state at the Fermi level.
   b) the magnetic phase transition drops from 335 K to $T_{c}=200$ K [5].

In this case the calculation of D.O. S by Wien 2K supports this idea (fig. 2 (b,c)).

2) It is difficult to estimate the magnetic ordering transition from $\rho(T)$ where a stronger concave curvature where the saturated part of Gd$_4$Bi$_3$ is more observable (pronounced) than Gd$_5$Bi$_3$ about $T \approx 100$ K where a small bump (main on DC-X) is visible.

Such behavior is presumed to be due to the short-range ordering effect through long-range interaction developed by the above suggestion "conduction electron concentration , c.e.c".

Consequently, if Gd$_5$Bi$_3$ is close to the critical value, near the double FM, AFM percolation threshold, it should be a point at which no frustration occurs, and then the system can be stabilized. This point has been found to be at $x/y=2$ where the system behaves completely para-magnetic as shown in fig. 3 (a). Thus the great exchange dispersion as well as magnetic ion site from Gd$_4$Bi$_3$ to Gd$_5$Bi$_3$ reflect the instability of both the magnetic and electrical character which are interchangeable with high value of $\mu_{\text{eff}}=8.34\mu_B$ at $x/y=5/3$. So the exchange interaction of magnetic ions are in conflict with each other and do
not allow the system to exhibit a long-range order (FM or AFM) but impose a new type of order at $x/y=2$. This point can be a minimized point in which the system is stabilized "physically" and metallurgical by completing of incomplete metallic bands to chemical covalent bond presented by the Kondo lattice behavior fig. 3 (b).

It will still be a question, whether the exchange interaction or distortion "band-deformation" is the main cause of this character, as both are functionals of $\Delta E_{s-d}$ in the Gd-IMC.

References

[1] T. Kasuya, O. Sakai, J. Tanaka, H. Kitazawa and T. Suzuki, J. Magn. Magn. Matter. 63& 64 (1987) 9.
[2] D. X. Li, Y. Haga, H. Shida, et. Al. J. Phys.: Condens. Matter 9 (1997) 10777-10788.
[3] A. Yazdani, J. ST. Gardner, Phys. Stat. sol. (b) 208 (1998) 465.
[4] Szade J. and Neumann M., J. Phys.: Condens. Matter 11 (1999) 3887.
[5] J. Szade, M. Drzyzga, J. Al. Comp. 299 (2000) 72-78.
[6] M. N. Abdusalyamova, A. G. Chuiko, E. I. Shishkin et. Al. J. Alloys Comp. 240 (1996) 272.
[7] K. Maeda, V. Vitek and A. P. Sutton, Acta. Metall. 30 (1982) 2001-2010.
Fig. 1: (a) Dependence of heat formation (melting point) on X concentration of magnetic ions Fermi surface (a) and Volume diagram (b) versus x/y for Gd$_x$Bi$_y$.
Fig. 2: (a) Temperature dependence of electrical resistivity for two Gd bismuthides (b) Total DOS for Gd$_5$Bi$_3$ (spin up) with LDA approximation (c) Total DOS for Gd$_5$Bi$_3$ (spin up) with GGA approximation

Fig. 3: Temperature dependence of the electrical susceptibility (a) and resistivity (b)