MAGNETIC PROPERTIES OF Fe, Co AND Ni IN LAVES PHASE BASED COMPOUNDS

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Overview:
1. Introduction
2. Itinerant electron magnetism
3. Laves phases
4. Magnetic properties
5. Conclusions
79 out of the 103 first elements are magnetic in their ground state
A few of them only are magnetic in the solid state
The 2 main series of magnetic elements

- Rare-earth element
- Transition-metal element

4f electrons: inner shell
3d electrons: outer shell

leads to very different behaviours
Magnetic Ordering

Paramagnetic

Ferromagnetic

Antiferromagnetic

Ferrimagnetic
Rare-earth (R)-transition metal (M) compounds

**Intrinsic R-M properties:**

- exchange interactions *(between all unpaired spins)*
- magnetocrystalline anisotropies
Rare-earth (R)-transition metal (M) compounds

Intrinsic R-M properties:
- exchange interactions (between all unpaired spins)
- magnetocrystalline anisotropies

Interactions:
- R-R (it’s the weakest, RKKY type)
- M-M (it’s the strongest)
- R-M
Exchange interactions in rare-earth metals

Magnetic 4f electrons localised
5d, 6s itinerant

4f moments coupled via
indirect RKKY interactions
RKKY interactions

\[ J_{RKKY}(R) \propto \frac{\cos(2k_F R)}{(2k_F R)^3} \propto \frac{1}{R^3} \]

4f

5d, 6s itinerant
Interaction between magnetic moments in R-M intermetallics

\[ S_{3d} \quad \text{AF} \quad S_{5d} \]

Hybridisation

Non - 4f moment

\[ M_M \quad M_R \]
Interaction between magnetic moments in R-M intermetallics

- Hybridisation
- Intra atomic coupling
- Spin-orbit coupling

Light rare-earth

S\text{3d}, S\text{5d}, S\text{4f}, L\text{4f}, M\text{M}, M\text{R}
Interaction between magnetic moments in R-M intermetallics

- Hybridisation
- Intra atomic coupling
- Spin-orbit coupling

Heavy rare-earth
Itinerant-Electron Magnetism

Ex: Metallic systems based on 3d transition elements

-3d electrons are responsible for magnetic properties
- we assume that the 3d bands are rectangular

N(E) remain constant over the whole energy range spanned by the bandwidth W
Schematic representation of a partially depleted 3d band

Paramagnetism
weak ferro.  strong ferro.  strong ferro.
with n > 5     with n < 5
Schematic representation of a partially depleted 3d band

Paramagnetism   weak ferro.   strong ferro.   strong ferro.
with $n > 5$ with $n < 5$

$U_{\text{eff}} N(E_F) > 1$  Stoner criterion
Susceptibility enhancement

\[ \chi = \frac{\chi_0}{1 - U_{\text{eff}} N(E_F)} \]

\[ [1 - U_{\text{eff}} N(E_F)]^{-1} \]

very high

Strong interaction between electrons

and/or

\( N(E_F) \) high
Susceptibility enhancement

\[ \chi = \frac{\chi_0}{1 - U_{\text{eff}} N(E_F)} \]

very high \[ [1 - U_{\text{eff}} N(E_F)]^{-1} \]

high \[ N(E_F) \text{ high} \]

metallic systems close to magnetic instability
LAVES PHASE COMPOUNDS

- $\text{YCo}_2$ exchange enhanced paramagnetism
- $\text{YFe}_2$ ferromagnetic
- $\text{YNi}_2$ paramagnetic
- $\text{YFe}_{2-x}\text{V}_x$ ferromagnetic
- $\text{YCo}_{2-x}\text{A}_x$; ($\text{A}=\text{Cr, Ti, V}$) exchange enhanced paramagnetism
- $\text{RM}_2$; ($\text{R}$=heavy rare earth, $\text{M}$=Fe, Co, Ni) ferrimagnetic
- $\text{GdCo}_{2-x}\text{A}_x$; ($\text{A}$=Si, Cu) ferrimagnetic
Laves phases

tetrahedrally close-packed alloys

3 types

MgCu$_2$  MgZn$_2$  MgNi$_2$
Laves phases

tetrahedrally close-packed alloys

3 types

MgCu$_2$  MgZn$_2$  MgNi$_2$

fcc – C15
Laves phases

tetrahedrally close-packed alloys

3 types

MgCu₂
  ↓
 fcc – C15

MgZn₂
  ↓
 hexagonal-C14

MgNi₂
Laves phases

tetrahedrally close-packed alloys

3 types

MgCu$_2$   MgZn$_2$   MgNi$_2$

fcc – C15   hexagonal-C14   hexagonal C36
The RM$_2$ Cubic Laves Structure (C15)

History: more than 20 years

Very interesting properties:

- variable moment on the M atom
- first order magnetic transition
- applied or molecular field induced metamagnetic transition

Interest:

- fundamental (simple crystal structure and intriguing characteristics –ideal for checking physical theories of magnetism)
- technical (hydrogen storage, refrigeration…)

R.Tetean; Chemnitz, Nov.2004
Hidrogen storage

The arrangement of hydrogen sites in C15 Laves phase compounds. The g and e sites are shown as circles and squares, respectively.

- At low hydrogen content, only the lowest energy sites (g sites) are occupied. These sites form a network of interpenetrating hexagons.
- As the hydrogen content is increased, the higher energy sites (e sites) also become occupied.
the magnetic entropy show maxima around Tc
-decrease with the increase of the Si content
-soft magnetically around Tc (magnetic hysteresis very small)

J.K. Singh et al., J. Appl. Phys, 2004
Metamagnetic transition

- magnetization not completely saturated
- with the increase of B the Fermi level of the minority band approaches the peak of the DOS and FM state occurs
- the metamagnetic transition is affected by spin fluctuations
- probably, MT affect the electronic structure of the d electron system

The MgCu$_2$ Cubic Laves Structure (C15)

Cu

Mg
Sample preparation

1. - arc melting
   - induction furnace
     - high purity ingots (better than 99.9 %)
     - small excess of Y or rare earth

2. - thermally treatment
   - several days
   - temperatures between 850-1000 °C
<table>
<thead>
<tr>
<th>Compound</th>
<th>Crystal structure</th>
<th>R=Fe (Å)</th>
<th>R=Co (Å)</th>
<th>R=Ni (Å)</th>
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<tbody>
<tr>
<td>GdM₂</td>
<td>MgCu₂</td>
<td>7,396</td>
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<td>TbM₂</td>
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<td>DyM₂</td>
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<td>HoM₂</td>
<td>MgCu₂</td>
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<td>ErM₂</td>
<td>MgCu₂</td>
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<td>TmM₂</td>
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<td>LuM₂</td>
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<td>YM₂</td>
<td>MgCu₂</td>
<td>7,363</td>
<td>7,216</td>
<td>7,182</td>
</tr>
</tbody>
</table>
MAGNETIC PROPERTIES

- temperature range 4.2-1000 K
- external magnetic fields up to 9 T

Spontaneous magnetizations:

\[ M = M_s \left( 1 - \frac{a}{H} \right) + \chi_0 H \]

Paramagnetic region

\[ \chi = \chi_p + \frac{cM'_s}{H} \]
Band structure calculation

- TB-LMTO-ASA (O.K. Anderson, O. Jepsen...)

Local density approximation:

Total electronic potential = sum of external, Coulomb and exchange correlation potentials (R.O. Jones, O. Gunnarson)

Functional form of the exchange-correlation energy:

Free electron gas parameterization (von Barth and Hedin)

Supercells used:

8 times greater than the unitary cell
- strong hybridization between 3d states (M) and 5d (4d) states of Y or R
- similarities in shape
- $U_{eff} N(E_F) = 0.21$ in YNi$_2$ (nonmagnetic)
- $= 2.6$ in YFe$_2$ (strong itinerant ferromagnet)
- $= 0.9$ in YCo$_2$ (exchange enhanced paramagnet)

MODELS

- Buschow ´71
  - R-M interactions RKKY-type

- Campbell ´72
  - 4f electrons of R polarize their 5d band
  - direct 5d-3d exchange interactions with M
  - 4f-5d (4d) exchange interactions are positive

- Brooks et.al. ´89, 91, 93
  - describe the 4f-5d exchange interactions by:

\[ H_{4f-5d} = -2J_{4f-5d} S_{4f} S_{5d} \]
- Li et al. '91
  - consider in addition $J_{4f-6s}$ and $J_{4f-6p}$

- Belorizky et al. '87
  - the decrease of $J_{4f-5d}$ is related to the radii variation of 5d and 4f shells

- Fähnle et al. '93
  - $J_{4f-5d}$ is important
  - no major contribution from $J_{3d-5d}$
The graph shows the magnetic moment (M) as a function of magnetic field (B) for YCo$_{1.875}$V$_{0.125}$ at different temperatures: T=300 K, T=180 K, T=75 K, and T=10 K. The magnetic moment decreases with increasing magnetic field. The materials YFe$_x$V$_{2-x}$ with different compositions x=1.8, x=1.6, and x=1.2 are also depicted with corresponding symbols on the right graph, showing similar trends.
$T_{\text{max}}(\text{LuCo}_2) = 370 \text{ K}$
$\mu_{\text{eff}}(\text{Co}) = 3.86 \mu_B/\text{atom}$

$T_{\text{max}}(\text{YCo}_2) = 260 \text{ K}$
$\mu_{\text{eff}}(\text{Co}) = 3.70 \mu_B/\text{atom}$

$T_{\text{max}}(\text{ScCo}_2) = 550 \text{ K}$
$\mu_{\text{eff}}(\text{Co}) = 3.92 \mu_B/\text{atom}$

\[ \chi = s \chi_p \left[ 1 + \frac{\pi^2}{6} \left( 2 \frac{N''}{N} - 1.2 \frac{N'^2}{N^2} \right) E_F \right] \]

\[ \chi \text{ (emu/mol 10}^{-3}) \]

\[ YCo_{1.9}Cr_{0.1} \]

\[ T^2 (K^2) \]

\[ \chi \text{ (10}^{-3} \text{ emu/mol}) \]

\[ YCo_{1.9}Ti_{0.1} \]

\[ T^2 (K^2) \]
E. Burzo, R. Tetean et al., J. Alloys. and Comp., 2001

$M_{\text{eff}} (\mu_B / \text{Co atom})$

$RCo_{2-x}Si_x$

- $R=Y$
- $R=Gd$

R. Tetean, et. al., J. Alloys and Comp., 2001
$M_{Fe} \approx 1.80 \mu_B/\text{atom}$

$M_{Co} \approx 1.00 \mu_B/\text{atom}$

$M_{Ni} \approx 0.00 \mu_B/\text{atom}$

R. Tetean et.al., Intermetallics, in press
\[ M_{5d} = M_{5d}(O) + aG \]
\[ M_{5d} = M_{5d}(O) + aG \]

\[ a = 2.1 \cdot 10^{-2} \mu_B \quad \text{independent on } M \]

\[ M_{5d}(0) = \begin{cases} 
0.02 \mu_B & M = Ni \\
0.27 \mu_B & M = Co \\
0.49 \mu_B & M = Fe 
\end{cases} \]

Two contributions:

- local 4f-5d exchange (the same for three series)

- \( M_{5d}(0) \) is dependent on M magnetic contribution (was attributed to the 5d band polarization as result of 5d-3d hybridization)
\[ M_{5d} = M_{5d}(O) + aG \]

\( M = \text{Ni} \)

- R5d polarization only 4f-5d exchange
- \( M \) is the same for a given \( R \), independent on \( M \)
- \( J_{4f-5d} \) little dependent on \( R \)

\( M = \text{Co or Fe} \)

- \( M_{5d}(0) \) increase as \( M \) moment increase
\[ M_{3d} = M_{3d}(O) + bG \]
\[ M_{3d} = M_{3d}(O) + bG \]

\[ b = \begin{cases} 
1.20 \cdot 10^{-2} \mu_B & M = Ni \\
1.90 \cdot 10^{-2} \mu_B & M = Co \\
2.00 \cdot 10^{-2} \mu_B & M = Fe 
\end{cases} \]

\[ M_{3d}(0) = \begin{cases} 
0.02 \mu_B & M = Ni \\
2.00 \mu_B & M = Co \\
3.60 \mu_B & M = Fe 
\end{cases} \]

\[ YFe_{2-x}V_x \]
\[ M_{V3d} \cdot M_{Y4d} \cdot M_{Gd5d} \ (\mu_B/\text{atom}) \]

\[ YFe_{2-x}V_x \]

\[ \text{GdCo}_{2-x}\text{Si}_x \]

\[ M_A (\mu_B/\text{f.u.}) \]

\[ \mu_B \]
CONCLUSIONS

• the exchange interaction parameters $J_{5d-3d}$ and for a given type of structure are nearly constant

• an identical ratio $M_{5d}(0)/M_{3d}(0)=0.12\pm(\pm)0.01$ in RCo$_2$ and RFe$_2$ series was shown. This suggest that the additional polarization is induced by 5d-3d short range exchange interactions

• the 5d-3d exchange interaction act like an internal field and increase the 5d band polarization

• the internal field quenched the spin fluctuation
FUTURE PROSPECTS

• ultra high magnetic field measurements
• measurements under high pressure
• electrical measurements
• consideration of 4f-6s, 4f.5d and 5d-5d interactions

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