Overview of the Polish partners
NAS-AMORE

Towards higher Curie temperatures in oxide materials

Work Package WP-A

New tools for improving the performance of double perovskite materials.

Contractor: IF PAN

Tasks:
KTA1 - NMR studies of $A_2FeMO_6$ (A=Sr, Ba, Ca), (M=Mo, Re)
  Key person: Dr Ewa Jędryka, Dr Marek Wójcik

KTA2 - New substrates for epitaxial growth of perovskite thin films.
  Key person: Dr Marek Berkowski
Overview of the Polish partners
NAS-AMORE

Work Package WP-B

Characterization of semiconducting magnetic oxides.
Contractors: IFPAN, IET

Tasks:

KTB1 - Theory of magnetic II-VI semiconductors
   Key person: Prof. T. Dietl

KTB2 - Characterization of semiconducting Zn-based oxides
   Key person: Prof. J. Kossut
Key Task KTA1 (NMR studies)

An extensive NMR study on samples provided by the consortium members.

• The role of Fe-Mo antisites (cooperation with ICMB)
• Electron doping by La substitution in $\text{Sr}_2\text{FeMoO}_6$ (cooperation with ICMB)
• W substitution in B sublattice of $\text{Sr}_2\text{FeMoO}_6$ (cooperation with TCD)
• Re NMR studies in $(\text{SrCa})_2\text{FeReO}_6$ (cooperation with TCD)
• Investigation of the low frequency structure in Mo NMR spectra by studies of $\text{Ba}_2\text{FeMoO}_6$ and $\text{Sr}_2\text{FeMoO}_6$ single crystal (cooperation with UPS).
Sr$_2$FeMoO$_6$ with varying Fe/Mo antisite concentration (in cooperation with ICMAB)

<table>
<thead>
<tr>
<th>Code</th>
<th>Ms (µB)</th>
<th>AS (from Ms) (1)</th>
<th>AS (from DRX) (2)</th>
<th>AS (from Rietveld) (3)</th>
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<tr>
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<td>2.8</td>
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<td></td>
<td>28</td>
</tr>
<tr>
<td>S104B</td>
<td>1.21</td>
<td></td>
<td></td>
<td>35</td>
</tr>
</tbody>
</table>

(1) From the measured magnetization: $Ms = 4\text{--}8AS$.  
(2) From the relative intensity of the order peak in XRD pattern.  
(3) From the XRD refinement (Rietveld method).

Correlation between saturation magnetization and AS content
**Sr$_2$FeMoO$_6$ with varying Fe/Mo antisite concentration** (in cooperation with ICMAB)

**Dramatic** effect of antisites on **macroscopic magnetic properties**: NMR restoring field scales perfectly with sample’s magnetic stiffness, both increasing by an order of magnitude between 3% and 28% AS concentration

- **Antiferromagnetic coupling** between Fe spins in regular sites and those in AS.

\[ H_{\text{stiff}} = \frac{1}{\chi_{\text{in}}} M_{\text{sat}}, \text{10 K} \]

\[ H_C, \text{10K} \]

\[ H_{\text{res}}, \text{4.2 K} \]

\[ A_1 = I_o \eta_1 \]

\[ A_2 = I_o \eta_2 \]

\[ H_{\text{rest}} = H_{hf} / \eta \]

\[ H_{\text{res, 1}} = \beta h_1 \text{ (Oe)} \]

\[ H_{\text{res, 2}} = \beta h_1 \text{ (Oe)} \]

\[ H_{\text{res}} = \beta h_1 \text{ (Oe)} \]

\[ S(H_1, \omega) = \eta \omega^2 I_0(\omega) \exp[-\log^2(H_1/H_{1\text{opt}})/2\sigma^2] \]


**Sr$_2$FeMoO$_6$ with varying Fe/Mo antisite concentration** (in cooperation with ICMAB)

**Microscopically,** $^{95,97}$Mo NMR spectra **not affected** by varying Fe/Mo AS content.

![Graph showing $^{95,97}$Mo NMR spectra](image)

**In general:**

$$HF = A_{\text{core}} \mu_{\text{local}} + A_{\text{cond}} \mu_{\text{local}} + A_{\text{tran}} \sum n_i \mu_{\text{neighbors}}$$

- $A_{\text{core}}$ - core s electrons
- $A_{\text{cond}}$ - conduction s electrons
- $A_{\text{tran}}$ - conduction s electrons (transferred hyperfine field).

**In SFMO** (no s electrons):

$$HF = A_{\text{core}} \mu$$

**Conclusion:** the on-site magnetic moment on Mo invariant with AS concentration
Electron doping by La substitution in A sublattice of SFMO (in cooperation with ICMAB)

**Substitution in A sublattice:**

- **Ca_{0.4}Sr_{1.6}FeMoO_6**
- **Sr_{2}FeMoO_6**
- **La_{0.2}Sr_{1.8}FeMoO_6**

20% of Ca^{2+} ions - **no change** of Mo hyperfine field distribution in SFMO

10% of La^{3+} ions - Mo NMR lines rapidly **shift upwards** but \textsuperscript{57}Fe NMR line (65.8 MHz) does **not change** its position.

Conclusion: Electron doping selectively enhances the magnetic moment on Mo site by adding electrons to spin polarized “spin down” conduction band.
Electron doping by La substitution in A sublattice of SFMO (in cooperation with ICMAB)

The gravity center of the $^{95,97}$Mo NMR spectrum correlates very well with samples’ Curie temperature, showing that they both depend critically on the same parameter: number of electrons in the conduction band.
Studies of W substitution in B sublattice of Sr$_2$FeMoO$_6$ (in cooperation with TCD)

**Isoelectronic substitution:**

Mo(Kr)$_{4d}5s^1$, Mo$^{(5+x)^+}$ ($4d^{1-x}$)

W(Xe)$_{4f}^{1}5d^46s^2$, W$^{(5+y)^+}$ ($5d^{1-y}$)

- Mo hyperfine fields: increases
- $^{57}$Fe hyperfine field - constant

The valence state of W differs from the valence state of Mo and is very close to W$^{6+}$ ($5d^0$)

Selective charge transfer between W and Mo.
Studies of W substitution in B sublattice of Sr$_2$FeMoO$_6$ (in cooperation with TCD)

The frequency shift and the lineshape of the main Mo line:
- **local environment effects.**
- **localized** character of charge redistribution in the B sublattice upon doping with W in SFMO.

$\nu(\text{Mo}) = \nu_0 + n_w \delta \nu$

$\delta \nu = 3.2 - 3.7 \text{ MHz}$, $\nu(\text{Mo}) = 115 \text{ MHz}$ with 12 W neighbors.

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Dublin, 23 September, 2003  
AMORE Final Meeting


$^{185,187}$Re NMR studies in \((\text{SrCa})_2\text{FeReO}_6\)

(in cooperation with TCD)

\begin{align*}
\text{Sr}_2\text{FeReO}_6
\end{align*}

\begin{align*}
\text{Mo hyperfine field (T)}
11 & 14 & 18 & 21 & 25 & 29 \\
95.97 & & & & & \\
\text{Mo NMR} & \text{in Sr}_2\text{FeMoO}_6
\end{align*}

\begin{align*}
\text{Re hyperfine field (T)}
94.8T & (933 MHz) \\
\text{Re NMR} & \text{in Sr}_2\text{FeReO}_6
\end{align*}

\begin{align*}
\text{Sr}_2\text{FeReO}_6
\end{align*}

\begin{align*}
\text{(SrCa)}_2\text{FeReO}_6
\end{align*}

\begin{align*}
\text{Mo hyperfine field (T)}
600 & 700 & 800 & 900 & 1000 \\
\text{Mo NMR} & \text{Sr}_2\text{FeMoO}_6 & \text{Sr}_{1.8}\text{Ca}_{0.2}\text{FeReO}_6 & \text{Sr}_{1.5}\text{Ca}_{0.5}\text{FeReO}_6
\end{align*}

\begin{align*}
\text{Re hyperfine field (T)}
24 T & (67 MHz) \\
94.8T & (933 MHz) \\
\text{Re NMR} & \text{Sr}_2\text{FeReO}_6
\end{align*}

\begin{align*}
\text{Spin Echo Intensity}
0 & 5 & 10 & 15 & 20 & 25 & 30 & 35 & 40 \\
\text{Frequency (MHz)}
600 & 700 & 800 & 900 & 1000
\end{align*}

\begin{align*}
\text{Mo(Kr)} & 4d^55s^1, \quad \text{Mo}^{(5+x)^+} (4d^{1-x}) \\
\text{Re(Xe)} & 4f^{14}5d^56s^2, \quad \text{Re}^{(5+y)^+} (5d^{2-y})
\end{align*}

\begin{align*}
0 - 25\% \text{ of Ca}^{2+} \text{ ions} \quad \text{progressive upshift} \text{ of Re hyperfine fields in (SrCa)}_2\text{FeReO}_6
\end{align*}

\begin{align*}
\text{HF(Re)} & = \mu_{\text{local}} ; \quad \text{HF(Re)/HF(Mo)} = 4
\end{align*}
Low frequency structure in Mo NMR spectra - \( \text{Ba}_2\text{FeMoO}_6 \) and \( \text{Sr}_2\text{FeMoO}_6 \) single crystal (UPS).

- not related to surface effects (NMR spectra identical in SFMO single crystal and in powder ceramics)

- not related to tetragonal lattice distortion

\( \text{BFMO} \quad \text{SFMO} \)

\( \text{Fe}^{5,v+} \quad \text{Mo}^{x+} \)

HF(Fe) increases

HF(Mo) increases
Conclusions

• Fe-Mo antisites do not influence hyperfine field distribution on Mo. The on site magnetic moment is the only source of hyperfine field on Mo and appears not to be affected by presence of antisites.

• Mo magnetic moment, related to spin polarization of the 4d electrons, is extremely sensitive to presence of additional electrons. They can be introduced into the system e.g. by La$^{3+}$ substitution for Sr$^{2+}$ or by altering the valence state of ions in the Mo sublattice by diluting it with W.

• The system has a tendency to accommodate these surplus electrons in the Mo 4d “spin down” orbitals, while not changing the charge on 3d Fe “spin down” states.

• In Sr$_2$FeReO$_6$ a similar effect of spin polarization of 5d Re states has been evidenced by preliminary Re NMR study.