The peculiarities of reduction and doping of vanadium oxides probed by TDPAC spectroscopy at ISOLDE

Speakers: A. Burimova, A. W. Carbonari, J. Schell
Local contacts: J. Schell, J. G. M. Correia
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Influence of valence of doping element on local electronic and crystal structure in vanadium oxides: Time-Differential Perturbed Angular Correlations spectroscopy at ISOLDE

Interest to vanadia is driven by its applications. Doping allows to tune the properties. New wave of battery-research ($\text{Zn}^{2+}/\text{H}_2\text{O}$):


A TDPAC + DFT study of dopant environment in $\text{V}_2\text{O}_5$ and VO$_2$ was proposed, it implied variation of dopant element and concentration

Available probe parents comprised $^{181}\text{Hf}$, $^{111}\text{In}$ (IPEN) and $^{111m}\text{Cd}$ (ISOLDE)
< 1 ppm: phase interplay

0.5+ at.%: doping type
< 1 ppm: phase interplay

0.5+ at. %: doping type
< 1 ppm: phase interplay

0.5+ at. %: doping type

---

Observations:

- Relaxation threshold near 823K
- Annealing in air, O₂, N₂ hinders relaxation
- Dynamic evacuation catalyzes relaxation
- Monochromatic interaction after relaxation
- Smooth reversible transition with temperature similar to that observed for other compounds, e.g. TiO₂
Working hypothesis:

Probe at V$^{4+}$ site in formed VO$_2$
Transition: $m$-VO$_2 \rightarrow t$-VO$_2$

Observations:

- Relaxation threshold near 823K
- Annealing in air, O$_2$, N$_2$ hinders relaxation
- Dynamic evacuation catalyzes relaxation
- Monochromatic interaction after relaxation
- Smooth reversible transition with temperature similar to that observed for other compounds, e.g. TiO$_2$

Objectives:

Eliminate the ambiguity concerning the observed site

Thus, elucidate the peculiarities of charge density distribution in the vicinity of the dopant

Thus, contribute to the understanding of reduction mechanism in vanadium oxides

Problem statement extended to:

What is the mechanism of reduction in V$_2$O$_5$?

- Topotactic
  \[ V_2O_5 \rightarrow VO_2 \]

- Consecutive
  \[ V_2O_5 \rightarrow V_6O_{13} \rightarrow VO_2 \]

- Comproportionation
  \[ V_2O_5 \rightarrow VO_2 \]
  \[ VO_2 + V_2O_5 \rightarrow V_6O_{13} \]

- Competitive
  \[ V_2O_5 \rightarrow VO_2 \]
  \[ V_2O_5 \rightarrow V_6O_{13} \rightarrow VO_2 \]
Objectives:

Eliminate the ambiguity concerning the observed site

Thus, elucidate the peculiarities of charge density distribution in the vicinity of the dopant

Thus, contribute to the understanding of reduction mechanism in vanadium oxides

Approach:

- TDPAC measurements with $^{111m}$Cd at intermediate temperatures: 473 - 873K
- Adapt the samples to enhance reduction*:
  - Thin films
  - Porous $V_2O_5$
- Include $V_6O_{13}$ blend to sample list
- Proceed with complementary DFT*

*in progress at home institution, infrastructure available
Objectives:

Eliminate the ambiguity concerning the observed site

Thus, elucidate the peculiarities of charge density distribution in the vicinity of the dopant (❖)

Thus, contribute to the understanding of the reduction mechanism in vanadium oxides

Argumentation:

Why TDPAC?
- XRD can be insensitive to parasitic phases at low concentrations; texture of $V_2O_5$ and oxygen deficiency induced defects add uncertainty to XRD analysis
- ND (used to probe the reduction of other compounds) is useless for vanadium
- Hyperfine methods allow the mapping of the local environment (❖)

Why ISOLDE?
- Catalytic effect of implantation induced defects on transition was detected
- Cd as a vacancy trap
- In contrast to $^{111}$In with associated aftereffect, $^{111m}$Cd may endow TDPAC spectra with info on relaxation dynamics in intermediate temperature range - of interest in reduction mechanism studies
< 1 ppm: phase interplay

0.5+ at.%: doping type
### Tested synthesis routes:
- Coprecipitation
- Solid state reaction route
- Hydrothermal synthesis
- Sol-gel
- Electric arc fusion of metallic vanadium and cadmium

### TDPAC with $^{111}\text{In}$ at home institution:

<table>
<thead>
<tr>
<th>Cd atomic fraction</th>
<th>site 1</th>
<th>site 2</th>
<th>site 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\nu_Q$, MHz</td>
<td>$\eta$</td>
<td>$\delta$, %</td>
<td>$\nu_Q$, MHz</td>
</tr>
<tr>
<td>&lt; 0.01</td>
<td>118.647</td>
<td>1</td>
<td>7.3</td>
</tr>
<tr>
<td>0.05</td>
<td>117.873</td>
<td>0.949</td>
<td>2.65</td>
</tr>
<tr>
<td>0.1</td>
<td>116.851</td>
<td>0.9442</td>
<td>0.93</td>
</tr>
</tbody>
</table>

XRD limitation

↓ substitution?
Tested synthesis routes:
- Coprecipitation
- Solid state reaction route
- Hydrothermal synthesis
- Sol-gel
- Electric arc fusion of metallic vanadium and cadmium

TDPAC with $^{111}$In at home institution:

<table>
<thead>
<tr>
<th>Cd atomic fraction</th>
<th>XRD limitation</th>
<th>site 1</th>
<th>site 2</th>
<th>site 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>v_Q, MHz</td>
<td>η, %</td>
<td>δ, %</td>
<td>v_Q', MHz</td>
<td>η, %</td>
</tr>
<tr>
<td>&lt; 0.01</td>
<td>118.647</td>
<td>1</td>
<td>7.3</td>
<td>109.331</td>
</tr>
<tr>
<td>0.05</td>
<td>117.873</td>
<td>0.949</td>
<td>2.65</td>
<td>108.581</td>
</tr>
<tr>
<td>0.1</td>
<td>116.851</td>
<td>0.9442</td>
<td>0.93</td>
<td>106.602</td>
</tr>
</tbody>
</table>
Pyrovanadate (Cd$_2$V$_2$O$_7$)

Metavanadate (CdV$_2$O$_6$)

Metavanadate phase transition

$\beta$-CdV$_2$O$_6$ $\rightarrow$ $\alpha$-CdV$_2$O$_6$

at $\sim$ 473K

M. Bosacka and A. Blonska-Tabero

Cd$_2$V$_2$O$_7$

0.5+ at. %: doping type

< 1 ppm: phase interplay

Objectives:

Identification of the well-defined sites

Thus, getting details on phase transition in cadmium metavanadate* and evolution of local environment with temperature

Thus, final classification of the doping

*to our knowledge, pioneer TDPAC and first transition mapping with hyperfine techniques in these compounds

Objectives:

Identification of the well-defined sites

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Approach:

- TDPAC measurements of CdV$_2$O$_6$ with $^{111m}$Cd probe at temperatures > RT: $300K^+$
- $^{111m}$Cd TDPAC of Cd$_2$V$_2$O$_7$: $RT^+$
- Fine fitting of dynamic interactions if any
- Full control over structure with XRD and other conventional methods†
- Full DFT analysis: $\beta$-CdV$_2$O$_6$, $\alpha$-CdV$_2$O$_6$, Cd$_2$V$_2$O$_7$

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*to our knowledge, pioneer TDPAC and first transition mapping with hyperfine techniques in these compounds

** 1023K+ range not explored

† the scope of equipment available at home institution was recently extended to Raman+SPM platform
Objectives:

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Argumentation:

- **Why vanadates?**
  - **Stoichiometric:** Essential components of vanadium slag processing. Understanding intrinsic properties ⇒ increase in the effectiveness of vanadium leaching and reduction of its environmental impact

- **Importance of $^{111m}$Cd probe**
  - Native element of cadmium vanadates
  - No aftereffect
  - Can express site selectivity different from $^{111}$In

- **$^{111m}$Cd source: implantation vs. irradiation**
  - $^{52}$V $\rightarrow$ $^{52}$Cr ⇒ sample contamination
  - Safety issues after irradiation ⇒ sample deactivation
Perspectives

Uncertainty of reduction mechanism, local environment issues, formation of oxoanions, etc, are actual questions not only for vanadium. We assume that the series extends to other oxides, including molybdenia and tungstenia.

Beam request

<table>
<thead>
<tr>
<th>Required Isotope</th>
<th>Implanted beam</th>
<th>Probe element</th>
<th>Type of experiment</th>
<th>Approx. Intensity (at/muC)</th>
<th>Target/Ion source</th>
<th>Required atoms per sample</th>
<th># of shifts</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{111m}$Cd (48m)</td>
<td>$^{111}$Cd</td>
<td>$^{111}$Cd</td>
<td>TDPAC</td>
<td>$10^8$</td>
<td>Sn target; VD 5 ion source</td>
<td>$2 \times 10^{10}$</td>
<td>4</td>
</tr>
<tr>
<td>$^{117}$Cd (2.49h)</td>
<td>$^{117}$Ag</td>
<td>$^{117}$In</td>
<td>TDPAC</td>
<td>$10^8$</td>
<td>UC target; RILIS (Ag) ion source</td>
<td>$5 \times 10^{10}$</td>
<td>2</td>
</tr>
</tbody>
</table>

Total # of shifts: 6

**TAC meeting:** complementary measurements ⇒ flexibility. Beam sharing with other groups possible, short-time beam use possible.
Supplementary Information
Examples of data obtained with $^{111m}$Cd

**Vanadia series**

**Starting point:** bulk (polycrystalline) $V_2O_5$

- **Sol-gel synthesized, annealed in air after implantation, TDPAC at RT**

- **Annealed with 5-5-5 route at 500°C, measured at RT**

- **Annealed with 5-5-5 route at 570°C, measured at RT**

**Note:** 5-5-5 = 5 mins air + 5 mins vacuum + 5 mins dynamic vacuum

- **Pure, measurement at 300°C in air**

- **Sol-gel measurement at 300°C in air**

- **Incident UV**

**Pure, commercial, measured at RT after annealing with 5-5-5 route at 570°C**

<table>
<thead>
<tr>
<th>Site #</th>
<th>f, %</th>
<th>$\nu_{Q2}$, MHz</th>
<th>$\eta$</th>
<th>$\delta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Site 1</td>
<td></td>
<td>83,3258</td>
<td>0.5445</td>
<td>0.0680</td>
</tr>
<tr>
<td>Site 2</td>
<td>91.5354</td>
<td>90.2028</td>
<td>0.0230</td>
<td>0.0215</td>
</tr>
</tbody>
</table>

**Pure, commercial, measured at 600°C**

**Similar to Naicker’s “VO$_2$”**

<table>
<thead>
<tr>
<th>Site #</th>
<th>f, %</th>
<th>$\nu_{Q2}$, MHz</th>
<th>$\eta$</th>
<th>$\delta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Site 1</td>
<td>100</td>
<td>77.0161</td>
<td>0.1802</td>
<td>0</td>
</tr>
<tr>
<td>Site 2</td>
<td>58.3614</td>
<td>90.2508</td>
<td>0.6119</td>
<td>0</td>
</tr>
<tr>
<td>Site 3</td>
<td>25.9731</td>
<td>96.5650</td>
<td>0.9999</td>
<td>0.0224</td>
</tr>
</tbody>
</table>

**Time invested in the adjustment of the post-implantation treatment necessary to reach probe relaxation**

Couldn’t get it with In-111!
Examples of data obtained with $^{111m}$Cd

“Vanadates” series

Nearest oxygen shells

Sites in metavanadate

In vanadium oxide

$d$

$<1 \text{ ppm Cd}$

$5\% \text{ Cd}$

$\text{CdV}_2\text{O}_5$

$t, \text{ ns}$
Previous findings: vanadia with TDPAC by Naicker et al.

! In $V_2O_5$, loss of physically absorbed water: $100^\circC$, loss of structural water: $340^\circC$

Naicker1993 and Naicker thesis, experimental details:
Probe: In-111 implanted at IONAS [phases attributed to $V_2O_5$]
Sample $[V_2O_5]$ annealed in vacuum at 870K for 1h:
$\nu_Q = 88.1$ MHz, $\eta = 0.62$ (f (fraction) ↑ with T)

Sample $[V_2O_5]$ annealed in air, 870K? for 0.5h:
$\nu_Q = 91.4$ MHz, $\eta = 0.61$ (smaller f, f ↓ with T)

Sample $[V_2O_5]$, measured at RT after annealing in vacuum in a sequence 923, 973K
$\nu_Q = 43.79$ MHz, $\eta = 0.329$ [attributed by Naicker to monoclinic? $VO_2$]

Sample $[VO_2]$, measured at 423K after implantation (in lower vacuum):
$\nu_Q = 89.15$ MHz, $\eta = 0.22$ [attributed by Naicker to rutile $VO_2$]
The reversibility of the transition in initially divanadium pentoxide probed with In-111:

The TDPAC spectra were taken after pre-annealing in vacuum and consequent probe relaxation!
Preliminary DFT results:

For Cd metavanadate in β-phase, obtained with Wien2k (APW+lo)

<table>
<thead>
<tr>
<th>Method</th>
<th>Site</th>
<th>Vzz, 10^21 V/m^2</th>
<th>eta</th>
<th>nuQ, MHz, V-S1</th>
<th>nuQ, MHz, Cd-111</th>
<th>[Vzz(Cd)-Vzz(V)]/Vzz(Cd)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBE, triclinic</td>
<td>Cd1</td>
<td>-28.41736</td>
<td>0.45079</td>
<td>-569.8476366</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>V1</td>
<td>6.55704</td>
<td>0.74418</td>
<td>7.624465116</td>
<td>131.4870117</td>
<td></td>
</tr>
<tr>
<td></td>
<td>V2</td>
<td>10.97877</td>
<td>0.342</td>
<td>12.76601163</td>
<td>220.1550791</td>
<td></td>
</tr>
<tr>
<td>PBE, monoclinic</td>
<td>Cd1</td>
<td>-6.00173</td>
<td>0.93851</td>
<td>-120.3514913</td>
<td>0.277816629</td>
<td></td>
</tr>
<tr>
<td></td>
<td>V1</td>
<td>4.33435</td>
<td>0.66119</td>
<td>86.91585368</td>
<td></td>
<td></td>
</tr>
<tr>
<td>WC, monoclinic</td>
<td>Cd1</td>
<td>5.93722</td>
<td>0.89003</td>
<td>119.0578852</td>
<td>0.2017594093</td>
<td></td>
</tr>
<tr>
<td></td>
<td>V1</td>
<td>4.73933</td>
<td>0.75448</td>
<td>5.51084837</td>
<td>95.03683662</td>
<td></td>
</tr>
<tr>
<td>LDA, monoclinic</td>
<td>Cd1</td>
<td>5.93436</td>
<td>0.7679</td>
<td>119.0005342</td>
<td>0.1438857771</td>
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<td></td>
<td>V1</td>
<td>5.08049</td>
<td>0.86838</td>
<td>5.907546512</td>
<td>101.8780499</td>
<td></td>
</tr>
</tbody>
</table>

For VO₂, DOS ok, but generally unsatisfactory results for EFG obtained with the Elk code (LAPW+lo)

<table>
<thead>
<tr>
<th>Sample</th>
<th>eta</th>
<th>Vzz, 10^21 V/m^2</th>
<th>Vzz ext, 10^21 V/m^2</th>
</tr>
</thead>
<tbody>
<tr>
<td>t-VO2</td>
<td>0.48</td>
<td>3.39</td>
<td>0.3941860465</td>
</tr>
<tr>
<td>m-VO2</td>
<td>0.96</td>
<td>2.01</td>
<td>0.2337209302</td>
</tr>
</tbody>
</table>

Next step - Hubbard term?