Diffusion in Intermetallic Compounds Studied Using Short-Lived Radioisotopes

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Diffusion

Study of diffusion important for the understanding and controlling of impurities in materials

- Control of useful/problematical impurities
- Activation energies
- Study of fundamental diffusion properties.

Already considerable programme of diffusion studies underway at ISOLDE: IS489.

Use of radiotracers using short and long-lived isotopes.
Radiotracer Technique (IS489)

Implantation

$^{111}\text{Ag}^+$

Used isotopes:

$^{111}\text{Ag}$, $^{67}\text{Cu}$, $^{24}\text{Na}$, $^{43}\text{K}$, $^{56}\text{Mn}$,
$^{59}\text{Mn}^{(59}\text{Fe})$, $^{65}\text{Ni}$, $^{61}\text{Mn}^{(61}\text{Co})$, $^{101}\text{Cd}^{(101}\text{Pd})$, $^{191}\text{Hg}^{(191}\text{Pt})$, $^{193}\text{Hg}^{(193}\text{Au})$

$\text{Cd}_x\text{Zn}_{1-x}\text{Te}$

$\varnothing = 6 \text{ mm}$

$d = 800 \mu \text{m}$

$550 \ldots 900 \text{ K}$

$30 \text{ nm}$

$60 \text{ keV}$

$\text{CdTe}$

$I\text{SOLDE CERN}$

$1 \ldots 30 \mu \text{m}$

$1 \ldots 30 \mu \text{m}$

$T_{\text{diff}} = 570 \text{ K}$

$t_{\text{diff}} = 30 \text{ min}$

$D_{\text{Ag}} = 7.6 \cdot 10^{-9} \text{ cm}^2/\text{s}$
What’s different about this work

Use of PAC (perturbed angular correlation) to examine the atomic nature of diffusion processes.

PAC very versatile technique (as evidenced by other proposals in this session)….but not usually used to study diffusion.

Study of intermetallic compounds:

• $L1_2$ compounds: $RIn_3$, $RGa_3$, $RSn_3$
• $Gd_3P_7$

Examine on a local scale some of the unusual diffusion behaviour associated with these compounds.

Tests last year during the Ag beamtime were encouraging.
Diffusion in solids

example: simple vacancy diffusion

\[
\text{rate} \propto \exp\left(- \frac{E_A}{k_B T}\right)
\]
Diffusion in intermetallic compounds

Only first-neighbor jumps allowed (?)

example: 6-jump cycle
Perturbed $\gamma\gamma$ Angular Correlation (PAC)

For diffusion experiments, monitor the changes of EFG as probe atoms move in the crystal.
Observing diffusion by PAC: Reorientation of EFG tensor

Heating increases jump frequency...

\[ g_2(t) \]

...first increases, then reduces relaxation.
PAC measurements of Cd jump rates in $L1_2$ structured compounds

- $R\text{In}_3$, $RGa_3$, $RSn_3$ with $R=$ rare earth
- $L1_2$ structure:

*Collins, Jiang, Bevington, Selim, Zacate, *PRL* 102, 155901 (2009) and refs. therein;
Jiang, Zacate, Collins, *Def. & Diff. Forum* 289-292, 725 (2009);
PAC measurements of Cd jump rates in $L1_2$ structured compounds

- $R\text{In}_3$, $R\text{Ga}_3$, $R\text{Sn}_3$ with $R$=rare earth

- Jump rates at phase boundaries:

<table>
<thead>
<tr>
<th>Jump rate larger for $R$-poorer boundary</th>
<th>Jump rate larger for $R$-rich boundary</th>
</tr>
</thead>
<tbody>
<tr>
<td>LaIn$_3$, CeIn$_3$, PrIn$_3$</td>
<td>LuIn$_3$, TmIn$_3$, ErIn$_3$, HoIn$_3$, DyIn$_3$, TbIn$_3$, GdIn$_3$</td>
</tr>
</tbody>
</table>

**divacancy or 6-jump mechanism**

**Simple vacancy mechanism**

RIn₃, RGa₃, RSn₃ with R=rare earth
Jump rates at phase boundaries indicate complex diffusion mechanism in light rare earth tri-indides
Possible explanation: constitutional defects differ in light and heavy R compounds

<table>
<thead>
<tr>
<th>Light R</th>
<th>Heavy R</th>
</tr>
</thead>
<tbody>
<tr>
<td>V_R and R_In</td>
<td>V_In and In_R</td>
</tr>
</tbody>
</table>

Aim of proposed experiments is to detect which defects are present across the RIn₃ series using ¹¹¹mCd
Why $^{111\text{m}}\text{Cd}$?

- Too few defects to be observed using $^{111}\text{In}$
- $^{111\text{m}}\text{Cd}$ is an impurity so that association between defects and Cd could enhance site fractions enough to determine defect configurations

Aim of proposed experiments is to detect which defects are present across the $R\text{In}_3$ series using $^{111\text{m}}\text{Cd}$

PAC measurements of Cd jump rates in $L1_2$ structured compounds*
Ga$_7$Pd$_3$

- One Pd site
- Two inequivalent Ga sites (3 & 4)

$^{111}$In/Cd in Ga$_7$Pd$_3$
- In/Cd only on Ga sites
- No defects observed
$^{111}$In/Cd in Pd$_3$Ga$_7$ (high temperature)

Damping of signal is due to loss in coherence among spin states as tracers jump

Diffusion and Defect Data 264, 27-32 (2007)
Cd jump rates in $\text{Ga}_7\text{Pd}_3$ – empirical analysis

$G_2(t) \cong \exp(-\lambda t)G_{2,\text{static}}(t)$

**Stochastic Model**

Seven distinct EFGs
- Three EFGs for Ga(3) site parameterized by quadrupole interaction frequency $w_Q(3)$
- Four EFGs for Ga(4) site parameterized by quadrupole interaction frequency $w_Q(4)$

Four EFG transition rates: $r_{3\rightarrow 3}$, $r_{4\rightarrow 4}$, $r_{3\rightarrow 4}$, and $r_{4\rightarrow 3}$

Initial fraction of probes on Ga(3) sites: $f_3$

Why difference in jump rates?


Diffusion and Defect Data 264, 27-32 (2007)
Cd jump rates in Ga₇Pd₃

- Scatter in the fits using stochastic model.
- Need to understand this better; Could perform DFT calculations, but experimental solution is more direct.

Proposal: repeat experiments using the $^{111m}$Cd probe and analyze using the stochastic model.

Use of $^{111m}$Cd allows elimination of $f_3$ in the model because of the principle of detailed balance:

$$f_3 \cdot 4r_{3 \rightarrow 4} = (1 - f_3) \cdot 3r_{4 \rightarrow 3}$$

This offers a unique opportunity to measure separately inter- and intra-sublattice jump rates.
## Beam request

### Table

<table>
<thead>
<tr>
<th>Isotope</th>
<th>T&lt;sub&gt;1/2&lt;/sub&gt;</th>
<th>Target</th>
<th>Yield (ions/µC)</th>
<th>Ion source</th>
<th>Shipping?</th>
</tr>
</thead>
<tbody>
<tr>
<td>111mCd</td>
<td>48 min</td>
<td>Sn</td>
<td>2×10&lt;sup&gt;8&lt;/sup&gt;</td>
<td>HP (VADIS)</td>
<td>No</td>
</tr>
</tbody>
</table>

- • 10 shifts split over 2-3 years.
- • Collections of ~ 15 mins allow many experiments to be performed over 3-4 day beamtime.
- • Easy to accommodate other groups.

### Work involved:

- • Need to determine “good” annealing temperatures for the compounds following implantation.
- • Ga<sub>7</sub>Pd<sub>3</sub> more focused, priority for 2011.
- • Large variety of L1<sub>2</sub> compounds to be examined, great flexibility.
Sample preparation

Option 1

\(^{111}\text{In in InCl}_3\) dissolved in HCl

Step 1: high purity metal foils folded together

Step 2: Arc melt at 45 DCA for \(~1\text{ sec}\)
Simple vacancy diffusion in $L1_2$ compounds

Simple vacancy jumps in $L1_2$

Simulating Simple Vacancy Diffusion in $L1_2$-Structured Compounds...

6-jump cycle $L1_2$
Ga sites in Ga$_7$Pd$_3$

Tracer jumps that lead to a change in EFG:

Ga(4) → Ga(4)  Ga(3) → Ga(3)  Ga(3) ↔ Ga(4)

Jump distances:

Ga(4)-Ga(4): 0.280 nm (×3) and 0.273 nm
Ga(3)-Ga(3): 0.310 nm (×4)
Ga(3)-Ga(4): 0.338 nm (×4)