Advanced Complex Hydrides: Development and Fundamental Studies of Promising New Hydrogen Storage Materials

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DOE FreedomCar Technical Targets
On-Board Hydrogen Storage System
(300 mile range - 5.6 kg H₂)

<table>
<thead>
<tr>
<th>Property</th>
<th>Units</th>
<th>Target</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen Density (gravimetric)</td>
<td>wt.% H</td>
<td>6</td>
</tr>
<tr>
<td>Energy Efficiency</td>
<td>%</td>
<td>97</td>
</tr>
<tr>
<td>Energy Density (volumetric)</td>
<td>W-h/L</td>
<td>1100</td>
</tr>
<tr>
<td>Hydrogen Density (volumetric)</td>
<td>kg H₂/m³</td>
<td>33</td>
</tr>
<tr>
<td>Specific Energy</td>
<td>W-h/kg</td>
<td>2000</td>
</tr>
<tr>
<td>Cost</td>
<td>$/kW-h</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>($/kg H₂)</td>
<td>(167)</td>
</tr>
<tr>
<td>Operating Temperature</td>
<td>°C</td>
<td>-40 - +50</td>
</tr>
<tr>
<td>Start-Up Time to Full Flow</td>
<td>sec</td>
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<tr>
<td>Hydrogen Loss</td>
<td>scc/hr/L</td>
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<tr>
<td>Cycle Life</td>
<td>cycles</td>
<td>500</td>
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<tr>
<td>Refueling Time</td>
<td>min</td>
<td>&lt;5</td>
</tr>
<tr>
<td>Recoverable Usable Amount</td>
<td>%</td>
<td>90</td>
</tr>
<tr>
<td>Composition</td>
<td>(H-Capacity)$_{rev}$</td>
<td>T for 1 atm. °C</td>
</tr>
<tr>
<td>-------------</td>
<td>----------------------</td>
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</tr>
<tr>
<td>AB$_2$-Type</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MmNi$<em>{4.5}$Al$</em>{0.5}$</td>
<td>0.58</td>
<td>0.83</td>
</tr>
<tr>
<td>LaNi$_5$</td>
<td>0.93</td>
<td>1.28</td>
</tr>
<tr>
<td>CaNi$_5$</td>
<td>0.55</td>
<td>0.99</td>
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<tr>
<td>AB$_2$-Type</td>
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<tr>
<td>Ti$<em>{0.98}$Zr$</em>{0.02}$V$<em>{0.43}$Fe$</em>{0.09}$Cr$<em>{0.05}$Mn$</em>{1.5}$</td>
<td>0.7</td>
<td>1.3</td>
</tr>
<tr>
<td>TiMn1.5</td>
<td>0.65</td>
<td>1.15</td>
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<tr>
<td>AB-Type</td>
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<td></td>
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<tr>
<td>TiFe</td>
<td>0.79</td>
<td>1.5</td>
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<tr>
<td>TiFe$<em>{0.85}$Mn$</em>{0.15}$</td>
<td>0.80</td>
<td>1.5</td>
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<tr>
<td>SS-Type</td>
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<td></td>
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<tr>
<td>(V$<em>{0.9}$Ti$</em>{0.1}$)$<em>{0.95}$Fe$</em>{0.05}$</td>
<td>0.95</td>
<td>1.8</td>
</tr>
<tr>
<td>A$_2$B Type</td>
<td></td>
<td></td>
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<tr>
<td>Mg$_2$Ni</td>
<td>1.23</td>
<td>3.3</td>
</tr>
<tr>
<td>Mg</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mg (MgH$_2$)</td>
<td>2.0</td>
<td>7.6</td>
</tr>
<tr>
<td>Mg (MgH$_{1.3}$)**</td>
<td>1.3</td>
<td>5.0</td>
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</tbody>
</table>

* In units of $10^{22}$ H-atoms/crystal cm$^3$
** RMC = Raw Materials Cost; US$/g$ H based on (H-Capacity)$_{rev}$
*** Hydro-Québec high-energy ball-milled
Metal Hydride Family Tree

Elements

Alloys

Solid Solutions

Intermetallic Compounds

- \(AB_5\)
- \(AB_2\)
- \(AB\)
- \(A_2B\)

Other

- \(AB_3\), \(A_2B_7\), \(A_2B_{17}\), etc.

Complexes

TM

- Borohydrides

Non-TM

- Alanates
- Amides
- Misc.

Other

- Polyhydrides

“Stable”

- Multiphase
- Quasicrystalline
- Amorphous
- Nanocrystalline

Metastable

Sandrock, JALCOM, 1999
Van’t Hoff Plots of Various Metal Hydrides

Enthalpy Values (kJ) Associated with the Processes Occurring During the Dehydrogenation of One Mole of NaAlH$_4$

\[
\begin{align*}
\text{NaH(s) + Al + 2 H}_2 & \quad 13.8^a \\
1/3 \beta\text{-Na}_3\text{AlH}_6(s) + 2/3 \text{Al} + \text{H}_2 & \quad 41.5 \\
1/3 \alpha\text{-Na}_3\text{AlH}_6(s) + 2/3 \text{Al} + \text{H}_2 & \quad 36.0 \\
\text{NaAlH}_4(l) & \quad 23.2^a \\
\text{NaAlH}_4(s) & \quad 56.5^b
\end{align*}
\]

Determination of NaAlD$_4$

Direct determination of hydrogen atom locations

<table>
<thead>
<tr>
<th>Atoms</th>
<th>295 K (pm)</th>
<th>8 K (pm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al–D (×4)</td>
<td>162.6(2)</td>
<td>162.7(2)</td>
</tr>
<tr>
<td>Na–D (×4)</td>
<td>243.1(2)</td>
<td>240.3(2)</td>
</tr>
<tr>
<td>Al–Na (×4)</td>
<td>261.8(1)</td>
<td>262.0(1)</td>
</tr>
<tr>
<td>Na–Na (×4)</td>
<td>275.0(1)</td>
<td>375.0(1)</td>
</tr>
<tr>
<td>Al–Al (×4)</td>
<td>353.4(1)</td>
<td>352.1(1)</td>
</tr>
<tr>
<td>Al–Al (×2)</td>
<td>107.3(1)</td>
<td>107.3(1)</td>
</tr>
</tbody>
</table>

Titanium Doping Enhances Dehydriding of NaAlH$_4$

Progress of hydrogen desorption in the course of time at different temperatures for samples of NaAlH$_4$: undoped and doped (2 mol% Ti(OBu)$_4$).

**Alane AlH₃**

\[ \text{AlH}_3 \rightarrow \frac{3}{2} \text{H}_2 + \text{Al} \]

- 10 wt % available \( \text{H}_2 \)
- Known for 40 years\(^1\)
- Controllable dehydrogenation at acceptable rates below 100 °C with additives\(^2\) or if ball milled\(^3\)
- Low (< 10 kJ/mol) \( \Delta H_{\text{dehy}} \) \( \Rightarrow \) very high pressures for charging at ambient or higher temperatures


Determination of the intrinsic and mechanically modified thermal stabilities of $\alpha$, $\beta$, and $\gamma$ alane (collaboration with Tohoku University)

Profiles of the three phases of AlH$_3$ before and after mechanical milling.

TG-DTA

Thermogravimetry and differential thermal analysis of the three phases of AlH$_3$ before and after mechanical milling.

Enthalpies of dehydriding reactions $\Delta H_{\text{dehyd.}}$ of the three phases of AlH$_3$.

Neutron Structure Determination of $\beta$ and $\gamma$ phases of AlH$_3$

$\beta$ phase

$\gamma$ phase


Borohydride $[\text{BH}_4^-]$

$$2 \text{LiBH}_4 + \text{MgH}_2 \rightarrow 4 \text{H}_2 + \text{MgB}_2 + 2 \text{LiH}$$

- Formation of kinetic product, MgB$_2$ prevents the formation of thermodynamic products, Mg and B.
- $> 9$ wt % $\text{H}_2$ reversible.
- High kinetic barrier necessitates $> 400$ °C for rapid dehydrogenation.

Effects of Ti-dopants on the kinetics of the dehydrogenation of MgH$_2$/2 LiBH$_4$

- TiCl$_3$ has a pronounced effect on the kinetics of the dehydrogenation of MgH$_2$/2 LiBH$_4$.
- No enhancement is observed during second cycle following rehydrogenation.
- Amount of rapidly released hydrogen has a linear relationship with amount of TiCl$_3$ added.
- Similar effects have been found with upon addition of TiCl$_3$ to LiBH$_4$ M. Au and A. Jurgensen J Phys. Chem. 2006, 110, 7062.

$\Rightarrow$ Kinetic effect is due to stoichiometric reaction between LiBH$_4$ and TiCl$_3$. 
Production of Diborane Upon Dehydrogenation of Novel Borohydrides

Dehydrogenation at 120 °C

Dehydrogenation at 100 °C

Dehydrogenation is Reversible IF second Step avoided
Hydrogen Storage via Reversible Dehydrogenation of Cycloalkanes

Dehydrogenation of NaAlH₄ at 120 °C

wt% H

uncatalyzed
Ti doped
polyhydride
new Ti catalyst

time (hours)
Mechanically Doped NaAlH$_4$

C.M. Jensen and R.A. Zidan, U.S. Patent 6,471,935 **2002**.
Maximization of hydrogen cycling performance of Ti-doped NaAlH₄

Dehydrogenation:
Rate of 1.8 wt % per hour observed at 100 °C for 2 mol % Ti-doped NaAlH₄ to Na₃AlH₆ is adequate to meet the demands of an onboard PEM fuel cell.

Cycling Tests of 2 mol % Ti-doped Na/Al

Re-hydrogenation

Barriers to Practicality

- Plateau Pressures of $\text{Na}_3\text{AlH}_6 / \text{NaH} + \text{Al}$ is too low.
- Rate of dehydrogention of $\text{Na}_3\text{AlH}_6$ to $\text{NaH} + \text{Al}$ is too slow.
- Heat management during re-hydriding of practical scale hydride beds
- Cycling Capacity of 3.0 - 4.0 wt % is too low.
- Dehydridng of other alanates (ie. $\text{LiAlH}_4$ and $\text{Mg(AlH}_4\text{)_2}$ ) are irreversible under $\text{H}_2$ pressure under moderate conditions.
Neutron Diffraction Structure Determination of Na$_2$LiAlD$_6$

Ccp array of [AlD$_6$]$^{3-}$ complex ions with Li filling the octahedral sites and Na filling the tetrahedral sites.

In situ Synchrotron XRD

⇒ Stepwise pathway also followed for rehydrogenation

J. Rijsenbeek, Y. Gao, C.M. Jensen, and S. Srinivasan submitted for publication
Cycling of NaAlH$_4$ doped with 2 mol % TiF$_3$

Cycling introduces shoulders on the Al XRD peaks

Rietveld refinements indicate that the shoulders correspond to a solid solution of Ti in Al of composition Al\textsubscript{0.93} Ti\textsubscript{0.07}.

Upon doping, the spectrum is dominated by a strong signal near zero-field. There is also a small signal with $g \sim 1.97$ that is quite similar to the Ti(III) signal that is observed in the TiF$_3$ doped sample. 5 Cycles. There is now a signal with $g = 2.01$ and $\Delta B_{pp} \sim 650$ G plus a signal near zero-field that is quite different from the original one. This spectrum is very similar to TiF$_3$ doped sample after 5 cycles.

After 10 cycles, only the Ti(0) signal near zero-field has largely disappeared and only the Ti(0) signal at $\Delta B_{pp} \sim 650$ G.
Tunneling and Scanning Electron Microscopy

Collaboration with Dr. C. Andrei and Prof. R. Holmstad, Norwegian University of Science and Technology

SEM image taken with backscattered electrons (BSE).

Energy Dispersive X-ray spectrum of a particle observed in uncycled NaAlH$_4$ doped with 2 mol % TiF$_3$ shows strong Ti and F peaks.

Small Angle Diffraction pattern of a Ti, F rich particle matches TiF$_3$.

TEM bright field image of a Ti, F rich particle observed in uncycled sample of NaAlH$_4$ doped with 2 mol % TiF$_3$.

High resolution image of TiF$_3$ grain. Indicated lattice planes were indexed as TiF$_3$. 
• No correlation between Al and Ti seen in the EDS maps directly after ball milling but correlation, suggesting Al-Ti bonding, seen after 15 cycles.

• No significant change in grain size after 15 cycles

Comparison of Ti K-edge XANES for samples doped with 2 mol % TiF$_3$ and a 3 cycle sample doped with 2 mol % TiCl$_3$ (green). These three samples have identical near-edge features, indicating the same Ti oxidation state.

J. Rijsenbeek, Y. Gao, C.M. Jensen, and S. Srinivasan submitted for publication
“$\text{Al}_3\text{Ti}$ forms immediately on doping with $\text{TiCl}_3$ and oxidation state is nearly invariant during hydrogen cycling” - J. Graetz, J.J. Reily, J. Johnson, A.Y. Ingatov, T.A. Tyson *Appl. Phys. Lett.* 2004 85, 500.

“$\text{Ti}(0)$ species are formed immediately on doping and state is nearly invariant during hydrogen cycling with $\text{TiCl}_3$. The formation of an alloy with Al or $\text{TiH}_2$ is *not* supported by EXAFS data.” - A. Leon, O. Kircher, J. Rothe, M. Fichtner, *J. Phys. Chem.* 2004 16372.
Only a relative minor change in the hydrogen cycling kinetics occurs whether the majority of titanium is Ti(III) or Ti(0).

⇒ the enhanced hydrogen cycling kinetics are due to a Ti species that is present in only a relatively minor amount.
Kinetic Studies: Elucidation of Rate Determining Step

Collaboration with Dr. T. Kiyobayashi, Institute for Advanced Science and Technology, Osaka Japan

- Dehydrogenation of Na$_3$AlH$_6$ is much slower than NaAlH$_4$ starting with Ti-doped NaAlH$_4$

- Dehydrogenation profiles can be closely simulated using rate constants determined from relative simple kinetic model

Relation between $N_{H_2}(t)$ and the rate constants $k_1$ and $k_2$

\[
\frac{N_{H_2}(t)}{N_{NaAlH_4}^0} = \left\{ 1 - \frac{k_2}{2(k_1 - k_2)} \right\} \{1 - \exp(-k_1 t)\} + \left\{ \frac{k_1}{2(k_1 - k_2)} \right\} \{1 - \exp(-k_2 t)\}
\]

- Assumed the two reversible dehydrogenation are first order and independent.
- Rate equations are treated as simultaneous differential equations
- Best fits obtained for $k_1 = 3.5 \times 10^{-3} \text{ s}^{-1}$ and $k_2 = 2.3 \times 10^{-5} \text{ s}^{-1}$
but directly Ti doped Na$_3$AlH$_6$ undergoes dehydrogenation at rates equal to that of Ti doped NaAlH$_4$!!

Dehydrogenation profiles at 110 °C of:
A) Ti-doped NaAlH$_4$
B) Ti-doped Na$_3$AlH$_6$
C) Zr doped NaAlH$_4$
D) Zr doped Na$_3$AlH$_6$

Dehydrogenation kinetics are not controlled by relative strengths Al-H bonds. ⇒ Kinetics are limited by processes long range atomic transport phenomenon and location of dopants

Eyring plots of rates constants for the dehydrogenation of
A) Ti doped NaAlH$_4$
B) Ti doped Na$_3$AlH$_6$
C) Zr doped NaAlH$_4$
D) Zr doped Na$_3$AlH$_6$

Enthalpies of activation, $\Delta H$ (kJ/mol) of Ti and Zr doped NaAlH$_4$ and Na$_3$AlH$_6$

<table>
<thead>
<tr>
<th></th>
<th>Ti doped</th>
<th>Zr doped</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaAlH$_4$</td>
<td>100 ± 7</td>
<td>134 ± 16</td>
</tr>
<tr>
<td>Na$_3$AlH$_6$</td>
<td>99 ± 13</td>
<td>135 ± 17</td>
</tr>
</tbody>
</table>
Infrared Spectroscopy

\[ \text{Al-H stretching frequency shifts} \Rightarrow \text{Al bonding is perturbed upon doping and/or ball milling.} \]

The $^1$H NMR spectrum NaAlH$_4$ consists of an expected broad component with a very long, 2000 sec, $T_1$ relaxation time and an anomalous sharp component with a short, 240 ms relaxation time indicating that it corresponds to highly mobile population of hydrogen. The sharp component is often ascribed to residual solvent BUT........

The $^2$H NMR spectrum of NaAlD$_4$ that is prepared in protio-solvents also contains a sharp component.

We have also eliminated the possibility that the sharp component is free H$_2$ gas as its spectrum consists of a resonance that is much narrower and has a $T_1$ of 13 msec.
Anelastic Relaxation

Prof. R. Cantelli, University of Rome

Long range component of the strain due to defects
Elastic dipoles $\lambda$ (hopping with time $\tau$)
Anelastic strain $\varepsilon^{\text{an}} = \lambda_1 n_1 + \lambda_2 n_2$
Stress $\sigma$: $dE_i = -\lambda_i \sigma$
Boltzmann distribution:
$$n_i = \exp \left(-\frac{E_i}{kT}\right)$$

Relaxation strength:
$$D = \frac{e^{\text{an}}}{e^{\text{el}}} \sim \frac{(\Delta\lambda)^2}{T}$$
Low Temperature Dependence of Elastic Energy Loss

A point-defect is formed during the dehydrogenation of the Ti-doped hydride that gives rise to a thermally activated relaxation process.

Experimental curve is much broader than predicted for a single Debye process.

⇒ At 70 K, the relaxing entities (very likely hydrogen) are strongly interacting and/or highly mobile, performing about $5 \times 10^3$ jumps/s (corresponding to an activation energy of 0.126 eV).

Anelastic spectroscopy has provided insight into the mechanism of the reversible dehydrogenation of Ti-doped NaAlH$_4$.

Observation of a deuterium isotope effect in the low temperature spectra shows that a mobilized population of hydrogen (defect hydride complexes) plays a fundamental role in the reversible dehydrogenation of NaAlH$_4$.

The formation of defect complex anions in concert with the formation of Na$_3$AlH$_6$ and takes place at much lower temperatures upon Ti doping of the hydride.

⇒ Ti atoms decrease the energy barrier to breaking the Al-H bonds.
Schematic representation of the proposed potential energy of H atoms in thermally treated NaAlH$_4$: (a) undoped and (b) Ti-doped. Minima correspond to: chemical bond sites (labelled as C), lattice sites coordinated with the titanium trap (T), interstitial sites (I), and vacancy sites (V). $E_R$ is the activation energy for vacancy relaxation (reorientation) and $E_C$, $E'_C$, $E''_C$ are the energies for H to break the bonds. $E_I$ is the activation energy for H interstitial migration, $E_B$ the binding energy of H to Ti.

Schematic representation of the proposed dehydrogenation model: a) AlH₄ group of initial NaAlH₄; b) products of thermal decomposition: formation of both AlH₆ and AlHₓ (x<6) units, segregated Al, interstitial H in free and Ti trapping sites. The H atoms migrating to the surface recombine as molecules and evolve as gas. c) H migration to the deepest trap (chemical bond) during a subsequent thermal treatment in which the decomposition reaction does not proceed significantly, and allows partial equilibrium to be reached.

Conclusions

- Alane is a very promising candidate for practical onboard hydrogen storage BUT a viable method for recharging must be developed.

- Borohydrides are promising candidates for practical onboard hydrogen storage but kinetic barriers to dehydrogenation and side reactions leading to the elimination of diborane must be overcome.
Conclusions

- EPR, synchrotron XRD, XAFS, and TEM studies indicate that for NaAlH$_4$ doped with 2 mol % TiF$_3$, the majority population of Ti changes from a Ti(III) species (TiF$_3$) to a Ti(0) species (Al$_3$Ti) during the first few cycles dehydrogenation-rehydrogenation.

- Only a relative minor change in the hydrogen cycling kinetics occurs whether the majority of titanium is Ti(III) or Ti(0). ⇒ the enhanced hydrogen cycling kinetics are due to a Ti species that is present in only a relatively minor amount.

- Infrared spectra show that mechanical milling with or without doping perturbs Al-H bonding.
Conclusions

• Ti dopants can enhance the kinetics of the dehydrogenation Na$_3$AlH$_6$ to rates similar to those that have been observed for Ti-doped NaAlH$_4$ suggesting that positioning of Ti rather than Al-H bond strengths limit dehydrogenation kinetics.

• Anelastic spectroscopy has detected highly mobile point-defects in heat treated Ti-doped hydride NaAlH$_4$ that involve hydrogen.
Acknowledgements

U.S. Department of Energy Hydrogen Program
Ministry of Economy, Trade, and Industry of Japan (METI) NEDO project WE-NET

Jensen Group
Reyna Ayabe  Allan Hee  Keeley Murphy  Dr. Sesha “Raman” Srinivasan
Celeb Brown  Walker Langley  Dr. Anne Richards  Martin Sulic
Lance Calnane  Brad Lewandowski  Aditya “Ashi” Savara  Dr. Dalin Sun
Todd Dalton  Meredith Kuba  Godwin Severa  Dr. Satoshi Takara
Dr. Chrystel Hagen  Dr. Christine Morales  Thomas Seidl  Dr. Ping Wang

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Dr. Ragaïy Zidan - Savanah River National Laboratory
Dr. Steven Guthrie, Dr. George Thomas, Dr. Karl Gross, Dr. Eric Majzoub - Sandia National Laboratory
Prof. Sandra Eaton - University of Denver
Dr. Tetsu Kiyobayashi, Dr. Nobuhiro Kuriyama, Dr. Hiroyoyuki Takeshita - National Institute for Advanced Industrial Science and Technology, Osaka, Japan
Dr. Kristin Kumashiro, Dr. Walter Niemczura - University of Hawaii
Dr. Hendrik Brinks, Prof. Bjorn Hauback, Dr. Arnulf Maeland - Institute for Energy Technology, Kjeller, Norway
Dr. Terry Udovic, Dr. Jorge Inguez, Tander Yildirim - National Institute of Standards and Technology
Prof. Klaus Yvon, Dr. Hans Hagemann, G. Renaudin, Sandrine Gomes - Université de Genève
Prof. Alberto Albinati - Università di Milano
Dr. Job Rijssenbeek, Dr. Yan Gao, G.E. Global Research Center
Prof. Rosario Cantelli, Oriele Palumbo, Annalisa Paolone - Università di Roma
Dr. Carmen Andrei, J. Walmsley, R. Holmestad - Norwegian University of Science and Technology

Spiritual Guidance
Dr. Gary Sandrock - Suna Tech
First dehydrogenation profiles at 150 °C for samples of NaH/Al + 4 mol % Ti powder mechanically milled for different periods

Comparison of the dehydrogenation Profiles of NaH/Al + 4 mol % Ti powder and NaAlH₄ + 4 mol % Ti both mechanically milled for 10h.

Relaxation process

- Elastic energy dissipation coeff.: $Q^{-1} = \frac{M''}{M'}$ from the decay of the vibration amplitude or from width of resonance curve.
- The maximum of the elastic energy loss occurs when the angular vibration frequency is equal to the relaxation rate of the mobile species.

$$d_x = \ln \left[ \frac{A(t)}{A(t+T)} \right]$$

Logarithmic decrement

Vibration amplitude

Time

Elastic energy loss

Temperature

$$Q^{-1} = \frac{M\nu_0(\lambda_1 - \lambda_2)^2n_1n_2}{T} \frac{1}{(\omega\tau)^\alpha + (\omega\tau)^{-\alpha}}$$