Resonant Ultrasound Spectroscopy Studies of Intermetallic and Quasicrystalline Hydrides

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Introduction

Resonant Ultrasound Spectroscopy (RUS):
A tool for condensed matter physics research.

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Presentation Outline

• Background Material
  – Review of elastic properties of solids
  – Resonant ultrasound spectroscopy (RUS)

• Motivation
  – Metal-Hydrogen (MH) systems

• Results
  – TaV$_2$H(D)$_x$ (Laves-phase hydride)
    • Ultrasonic attenuation due to H motion
    • Anomalous hydrogen-dependent elastic properties

• Summary

• Nano-structured Materials at Forschungszentrum Karlsruhe
  – Elastic and anelastic properties??
Elastic Properties of Solids

• Generalized Hooke’s law:

$$\sigma_{ij} = C_{ijkl} \varepsilon_{kl}, \quad \varepsilon_{ij} = \frac{1}{2} \left( \frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right), \quad C_{ijkl}^S = \frac{\partial^2 U}{\partial \varepsilon_{ij} \partial \varepsilon_{kl}}$$

Strain tensor ($u_i$ components of displacement vector)

• Elastic constants are related to…
  – Thermodynamic properties of the material (Debye theory)
  – Interatomic forces
  – Practical (engineering) moduli (Young’s, shear, bulk) and Poisson’s ratio
  – Phase transitions
Symmetry to the Rescue!

- Symmetry arguments lead to 6-d formalism

\[ \sigma_{\alpha} = C_{\alpha\beta} \varepsilon_{\beta} \]

(Where \( \alpha \) and \( \beta \) = 1, 2, 3, 4, 5, 6)

- Crystal symmetry
  - Further reduces number of independent elastic constants
  - Polycrystalline materials often elastically isotropic
    - 2 independent elastic constants

For anisotropic crystal:

\[
C_{\alpha\beta} = \begin{pmatrix}
\lambda + 2\mu & c_{12} \lambda & c_{13} & 0 & c_{14} & \mu & c_{16} \\
\lambda & \lambda + 2\mu & c_{22} \lambda & 0 & c_{24} & \mu & c_{26} \\
& \lambda & \lambda + 2\mu & c_{33} + 2\mu & 0 & \mu & c_{36} \\
0 & c_{14} & c_{24} & 0 & c_{44} & \mu & c_{46} \\
0 & c_{15} & c_{25} & 0 & c_{45} & 0 & c_{56} \\
0 & c_{16} & c_{26} & 0 & c_{46} & 0 & c_{66}
\end{pmatrix}
\]
Ultrasonic Attenuation in Solids

- Exponential decrease of sound intensity with propagation due to coupling of ultrasonic vibrations with...
  - Thermal phonons
  - Conduction electrons
  - Dislocations / point defects
  - Coupling to the ‘order parameter’ of a phase transition

- **Relaxation-attenuation effects**
  - Re-orientation / hopping of a defect or light interstitial under the influence of strain
The Anelastic Solid

- Time delay between application of stress and resultant strain
  - Introduce relaxation time $\tau_R$
    \[
    \sigma + \tau_R \frac{d\sigma}{dt} = c_R \epsilon + \tau_R c_U \frac{d\varepsilon}{dt}
    \]
  - Frequency-dependent complex elastic constant
    \[
    c^*(\omega) = c_U + \frac{c_R - c_U}{1 + \omega^2 \tau_R^2} + i(c_U - c_R) \frac{\omega \tau_R}{1 + \omega^2 \tau_R^2}
    \]
Relaxation Attenuation

• Derive expression for ultrasonic loss

\[ \frac{1}{Q} = \left( \frac{\Delta c}{c} \right) \frac{\omega \tau_R}{1 + \omega^2 \tau_R^2} \], \quad \Delta c = c_U - c_R

  – Represents a Debye-time relaxation function
  – \( \Delta c/c \) = relaxation strength
  – \( c_U \) and \( c_R \) are the unrelaxed and relaxed elastic constants respectively

• Derive expression for associated shift in resonant frequencies

\[ \delta f = \left( \frac{\Delta c}{c} \right) \left( \frac{f}{2} \right) \frac{\left( \omega \tau_R \right)^2}{1 + \omega^2 \tau_R^2} \]
The Two-Level-System (TLS)

- Model H-motion in a material by considering a TLS
  - H atom occupies one of two adjacent sites
  - Parameter $A$ denotes site asymmetry
  - Tunneling matrix element, $\Delta_0$, denotes the overlap of wave functions from two sites
  - Energies of system are, $E = \pm (\Delta_0^2 + A^2)^{1/2}$
  - Relaxation strength given by,

\[
\frac{\Delta c}{c} = \frac{nD^2}{k_B T c} \left[ \frac{A}{E} \right] \text{sech}^2 \left[ \frac{E}{k_B T} \right]
\]

\[
D = \frac{\partial (\Delta E)}{\partial \varepsilon}
\]

Deformation Potential
Resonant Ultrasound Spectroscopy (RUS)

• Excite vibrational eigenmodes of samples of well defined geometry
  – Frequencies are function of sample dimensions and shape, density, crystal symmetry, and the $c_{ijkl}$
  – Compute numerically resonant frequencies of a well-defined sample\textsuperscript{1,2}
  – Derive full elastic constant tensor from single mechanical resonance spectrum

• Internal friction, $Q^{-1}$, determined from linewidth
  – In principle can determine internal friction matrix, $Q_{ij}^{-1}$

\textsuperscript{1}I. Ohno, J. Phys. Earth \textbf{24}, 355 (1976)
\textsuperscript{2}A. Migliori \textit{et al}. Physica B \textbf{183}, 1 (1993)
Resonant Ultrasound Spectroscopy (RUS)

- Sample-transducer assembly: He4 cryostat

![Diagram of sample-transducer assembly: He4 cryostat]

- Transducer housing
- Sample

Approximately 1 mm
Resonant Ultrasound Spectroscopy (RUS)

Typical RUS spectrum: TaV$_2$H$_{0.06}$

$T = 100.1$ K
Fitting the RUS Spectra

• Required for high-accuracy, especially for small, highly attenuating samples at low T

\[ S_{RUS} = \frac{A e^{-i\theta}}{(f_0^2 - f^2) - i(f_0 f / Q)} + \left[ b_1 + i b_2 + (c_1 + c_2)(\frac{f - f_0}{f_0}) \right] \]

Lorentzian lineshape

Detect and fit both in-phase and quadrature signals

Diagram:
- TaV₂D₅.17
- Q = 1054
- \( f_0 = 0.716900 \) MHz
- T = 204.8 K
Ultrasonic attenuation and dispersion due to hydrogen motion in the C15 Laves-phase compounds TaV$_2$H(D)$_x$
Metal-Hydrogen Systems

• Technological Interest
  – Hydrogen storage materials
  – Ni/MH re-chargeable batteries
  – Fuel-cell technologies
  – Hydrogen induced embrittlement of metals
  – Reversible mirrors and magnets

• Theoretical Interest
  – Diffusion of a light interstitial: classical versus quantum effects?
  – Electronic and magnetic effects
  – Thermodynamics
  – Lattice defects / strain
  – Vibrational modes
C15 Laves-phase: Crystal Structure

- $\text{TaV}_2$
  - Green spheres represent Ta atoms
  - Red spheres represent V atoms

- $\text{TaV}_2\text{H(D)}_x (x \leq 1.7)$
  - Absorbs and desorbs H
  - Solid-solution phase

- H occupies interstitial sites

C15 Laves-phase $\text{AB}_2$: Interstitial Sites

- Red – “g” sites
  (2 A and 2 B atoms)
- Green – “e” sites
  (1 A and 3 B atoms)
- Hydrogen usually occupies the “g” sites

(Figure courtesy of Dr. G. Majer, Max Planck Institute, Stuttgart, Germany.)
Why investigate TaV\textsubscript{2}H(D)\textsubscript{x}? 

Two frequency scales of H motion

Vacant g sites
H

I. “slow”
II. “fast”

\( \omega \tau = 1 \)
Why do internal friction measurements??

- Ultrasound measurements complementary to NMR and QENS measurement techniques
  - Explore different time-scales
  - Isotope effect
  - Couples to H motion differently

- Little or no previous work using ultrasound to explore H motion in C15 intermetallic compounds
Internal Friction: TaV$_2$H$_x$

Ultrasonic loss (1/Q) vs Temperature (K)

Peak maximum where, $\omega \tau = 1$

$\text{TaV}_2\text{H}_x$

All modes
$\approx 99\% C_{44}(G)$

$f_n \approx 1 \text{ MHz}$

$\text{TaV}_2\text{H}_x$

$\approx 0.53$

$\approx 0.34$

$\approx 0.18$

$\approx 0.10$

$\approx 0.06$

$\approx 0.06$

$\approx 0.00$
Internal Friction: $\text{TaV}_2\text{H}_{0.34}$ and $\text{TaV}_2\text{H}_{0.53}$

- Data for $x > 0.18$ require single Arrhenius-type relaxation time

\[
\frac{1}{Q} = \left( \frac{\Delta C}{C} \right) \frac{\left( \omega \tau_R \right)}{1 + \omega^2 \tau_R^2} \quad \tau_R = \tau_0 \exp \left( \frac{E_A}{k_B T} \right)
\]

- $\text{TaV}_2\text{H}_{0.34}$
  - $E_A = 0.22 \text{ eV}$
  - $\tau_0 = 5.7 \times 10^{-12} \text{ s}$
  - $f = 0.68 \text{ MHz}$
  - $f = 0.82 \text{ MHz}$
  - $f = 1.20 \text{ MHz}$

- $\text{TaV}_2\text{H}_{0.53}$
  - $E_A = 0.23 \text{ eV}$
  - $\tau_0 = 3.9 \times 10^{-12} \text{ s}$
  - $f = 0.64 \text{ MHz}$
  - $f = 0.87 \text{ MHz}$
  - $f = 1.64 \text{ MHz}$
Dispersion and Attenuation: TaV$_2$H$_x$

- Relaxation causes frequency dependent shift in real part of elastic constant

\[ \delta f = \left( \frac{\Delta C}{C} \right) \left( \frac{f}{2} \right) \left( \frac{\omega \tau_R}{1 + \omega^2 \tau_R^2} \right) \]

In novel approach both ultrasonic loss and frequency data fitted using same parameters for H motion.
Results Summary: TaV$_2$H$_{0.34}$ and TaV$_2$H$_{0.53}$

- Favourable comparison of parameters derived by RUS and NMR
  - Slower long-range (hex to hex) hopping mechanism

<table>
<thead>
<tr>
<th>Sample</th>
<th>Activation energy $E_A$ (eV)</th>
<th>Relaxation Time $\tau_{R0}$ (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(RUS) TaV$<em>2$H$</em>{0.34}$</td>
<td>0.22</td>
<td>5.7 E-12</td>
</tr>
<tr>
<td>(RUS) TaV$<em>2$H$</em>{0.53}$</td>
<td>0.23</td>
<td>3.9 E-12</td>
</tr>
<tr>
<td>(NMR) TaV$<em>2$H$</em>{0.22}$</td>
<td>0.23</td>
<td>2.5 E-12</td>
</tr>
<tr>
<td>(NMR) TaV$<em>2$H$</em>{0.56}$</td>
<td>0.24</td>
<td>1.1 E-12</td>
</tr>
</tbody>
</table>
Internal Friction: TaV$_2$H$_{0.06}$

• Data for $x \leq 0.18$ could not be fit by single Arrhenius expression

\[
\tau_i = \tau_{oi} \exp\left(\frac{E_i}{k_B T}\right) \quad (i = 1, 2) \quad \rightarrow \quad \tau_R^{-1} = \tau_1^{-1} + \tau_2^{-1}
\]

![Graphs showing ultrasonic loss (1/Q) versus temperature (K) for TaV$_2$H$_{0.06}$ at different frequencies.](image)
Internal Friction: \( \text{TaV}_2\text{H}_{0.10} \) and \( \text{TaV}_2\text{H}_{0.18} \)

- Data for \( x \leq 0.18 \) fit by two Arrhenius rates
Results Summary: TaV$_2$H$_x$, $x \leq 0.18$

- Data for $x \leq 0.18$ could not be fit by single Arrhenius expression

<table>
<thead>
<tr>
<th>Sample</th>
<th>$E_{A1}$ (eV)</th>
<th>$E_{A2}$ (eV)</th>
<th>$\tau_{01}$ (s)</th>
<th>$\tau_{02}$ (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TaV$<em>2$H$</em>{0.06}$</td>
<td>0.27</td>
<td>0.08</td>
<td>6.2 E-13</td>
<td>5.0 E-09</td>
</tr>
<tr>
<td>TaV$<em>2$H$</em>{0.10}$</td>
<td>0.28</td>
<td>0.10</td>
<td>5.2 E-13</td>
<td>11.0 E-09</td>
</tr>
<tr>
<td>TaV$<em>2$H$</em>{0.18}$</td>
<td>0.27</td>
<td>0.12</td>
<td>9.6 E-13</td>
<td>6.0 E-09</td>
</tr>
</tbody>
</table>

For Ta$_2$: Debye temperature $\Theta_D \approx 250$ K, Debye frequency $\omega_D \approx 6 \times 10^{12}$ s$^{-1}$
(c.f. $\tau_{01}^{-1} \approx 1$-$2 \times 10^{12}$ s$^{-1}$)
Relaxation Rates and Processes

Tunneling through ground state (process 2), may be suppressed at higher H concentrations due to lattice expansion.

\[ \tau_R^{-1} (s^{-1}) \]

\[ \frac{1000}{T} (K^{-1}) \]

\[ \text{TaV}_2\text{H}_x \]
Relaxation Strength: Snoek Relaxation

- Find $\Delta c$ is linear in H concentration $n$

$$\frac{\Delta c}{c} = \frac{nD^2}{k_B T c}$$

- From RUS experiments derive value for $D$

Experimental verification of Snoek effect for H in an intermetallic compound

$D = 0.17$ eV
Isotope Effect: \( \text{TaV}_2\text{H}_{0.18} \) and \( \text{TaV}_2\text{D}_{0.17} \)
Low-T Internal Friction: TaV$_2$D$_{0.17}$

- Peaks observed for all modes of TaV$_2$D$_{0.17}$
  - Associated with rapid local motion of D
  - Non-Arrhenius behavior

- Other form of relaxation time!

$$\tau_L = \tau_{L0} \exp\left(-\frac{T}{T_0}\right)$$

- Estimate fraction of D atoms participating in local motion

$$n_l = 3 \times 10^{-3} n_h$$
Low-T Shear Modulus: TaV$_2$D$_{0.17}$ / TaV$_2$H$_{0.18}$

- Resonant tunneling can lead to decrease in sound velocity
  - Relaxation rate determined by tunneling matrix elements $\Delta_H (\Delta_D)$
  - Magnitude of effect depends on $\Delta_0^2$
  - Expect $\Delta_H >> \Delta_D$

$$\Delta C_{H,D} = -\frac{nD^2\Delta^2_{H,D}}{E^3} \tanh \left[ \frac{E}{k_B T} \right]$$

Modulus effect larger for H but relaxation attenuation not observed as H motion remains too rapid
Summary: H(D) motion in TaV$_2$H(D)$_x$

- Two frequency scales of motion clearly resolved

- Low-temperature internal friction peak (intra-hexagon hopping)
  - Corresponds to “fast motion” seen in NMR and QENS
    - Hopping within hexagon of “g” sites
  - Non-Arrhenius behavior
  - Strong isotope effect (peak not observed for H) suggest tunneling motion
  - Appears H hopping rate $>>$ 1 MHz down to 3 K

- High-temperature internal friction peak (inter-hexagon hopping)
  - Distributions not required to fit results
  - Suggestive of tunneling through ground state and excited state
  - $\Delta C$ linearly dependent on H concentration – Snoek-type relaxation
Strong-hydrogen related effects on the shear elastic modulus of the C15 Laves-phase compounds TaV$_2$H(D)$_x$
Elastic Constants: Temperature Dependence

- Lattice and electronic contributions to $U$ or $F$
  - Thermal expansion also plays a role
  
  \[
  C_{ijkl}^S(T) = C_{ijkl}^0 + \left[ \frac{\partial^2 U_e}{\partial e_{ij} \partial e_{kl}} \right] + \left[ \frac{\partial^2 U_{\ell}}{\partial e_{ij} \partial e_{kl}} \right] + \frac{dC_{ijkl}^0}{dV} \Delta V(T)
  \]

- In many cases:
  - Electronic effects $\propto T^2$, often negligible
  - Lattice effects $\propto T^4$ at low $T$, $\propto T$ at high $T$

Situation changed by unusual electronic structure or phase transitions

Example: Cu

Bulk modulus $K$ (GPa)

Temperature (K)
Shear Modulus: C15 Laves Materials

• C15 Laves-phase intermetallics (TCP materials)
  – High m.p. temperatures and relatively low densities
Shear Modulus: C15 Laves Materials

- Anomalous elastic properties also observed in other C15 Laves-phases
  - HfV$_2$ and ZrV$_2$ show stiffening in shear and Young’s moduli with *increasing T* from ~ 120 K to m.p.$^1$

- Results described by an electronic band-structure model$^{2,3}$
  - Typically addition of H to metal raises Fermi Level
  - Could elastic properties of TaV$_2$ be affected by additional H??

Shear Modulus: TaV$_2$H$_x$, 0 $\leq$ x $\leq$ 0.54
Shear Modulus: \( TaV_2H_x, \quad 0 \leq x \leq 0.10 \)
Relaxed Shear Modulus: TaV$_2$H$_x$, $0 \geq x \leq 0.54$
Overview of Theoretical Model

• Symmetry of C15 lattice leads to doubly-degenerate electronic energy levels at X point of IBZ
  - Linear dispersion

\[ E_{1,2} = \pm \sqrt{s k_{1,2}^2 + D^2 e_4^2} \]

• Helmholtz free energy of system of N electrons

\[ F = N E_F - 2 \sum k_B T \ln \left[ 1 + \exp \left( \frac{E_F - E_{bk}}{k_B T} \right) \right] \]

Expect unusual effects if \( E_F \) lies near double-degeneracy level!
Overview of Theoretical Model

- Calculate $G(T, x)$ based on this electronic model

$$G(T, x) = C_{bg} (T) - K \int_{0}^{\Omega} \frac{d\varepsilon}{\varepsilon} \left[ \frac{\sinh(\varepsilon / k_B T)}{\cosh(\varepsilon / k_B T) + \cosh(E_F / k_B T)} \right]$$

- For $C_{bg}(T)$ utilize the semi-empirical Varshni Model

$$C_{bg} (T) = C_o - \frac{S}{\exp \frac{t}{T}} - 1$$

Same background, for all $x$
Comparison of Model to Experimental Data

Calculated $G(T)$ for various $E_F$ (K)

Experimentally determined $G(T)$ for various H concentrations
Theoretical Model: Some Conclusions

• For TaV$_2$, $E_F$ lies very near double-degeneracy level (~ 2 meV)

• Addition of H shifts $E_F$ away from this level
  - Is shift compatible with electronic DOS of TaV$_2$H$_x$??

• NMR measurements$^1$ show linear decrease of $N(E_F)$ vs. $x$ over $x$ range of present measurements!!
  - Use NMR-derived $N(E_F)$ to calculate shift

$$E_F = \int_0^x \frac{fdx'}{N(E_F, x')}$$

$f$ = fraction of an electron added at Fermi level due to each H atom

A.V. Skripov, J. Alloys and Compd, 177, 63 (1991)
Theoretical Model: More Conclusions

• Results in good agreement?
  - Each H atom donates \( \approx 1 \) electron
  - \( E_F \) lies very near double-degeneracy point in TaV\(_2\) (\( \approx 2 \) meV)
  - Addition of H shifts \( E_F \) away from this level

\[ f = 1 \]
Theoretical Model: Conclusions

• Discrepancy?
  - Calculations\(^1\) indicate that for TaV\(_2\) \(E_F \approx 1000\) K above double-degenerate levels??

• Simple model may still apply
  - Perhaps it is not the X-point which is responsible for softening in aggregate shear modulus
  - Single crystal measurements required
  - We found bulk modulus \(K(T)\) only weakly dependent on temperature

\[
K_V = \left( c_{11} + 2c_{12} \right) / 3 \\
G_V = \left( c_{11} - c_{12} + 3c_{44} \right) / 5
\]

\(^1\)F. Chu et al. Phil Mag. B 70, 867 (1994)

Voigt averages for a polycrystalline material containing cubic crystallites
General Conclusions

• Observed remarkable hydrogen-related electronic effect for shear modulus of TaV$_2$H$_x$

• Magnitude and temperature dependence highly dependent on $x$
  - Hydrogen to ‘tune’ elastic properties of Laves-phase materials?

• Results in good agreement with model detailing electronic contributions to single-crystal $c_{44}$

• Increase in $E_F$ determined from elastic constant and NMR data in remarkable agreement

• Results indicate that H contributes approximately one electron to conduction band at Fermi level
Summary

• RUS has been used to make high quality ultrasonic loss and elastic constants measurements of TaV_{2}H(D)_{x} between 0.3 - 345 K
  - Loss and dispersion results used to derive parameters of H diffusion
  - Strong isotope effect on rapid local H(D) motion

• Remarkable electronic hydrogen-related effects on $G(T)$

• Use of ultrasound for exploring H motion in intermetallics has been extended

• Results extremely difficult to obtain with other acoustic techniques
Acknowledgments

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