2008 Hydrogen and Helium Isotopes in Metals Conference
Albuquerque, NM
February 6, 2008

Ultrasonic Study of Hydrogen Short-Range Ordering in Palladium Hydride

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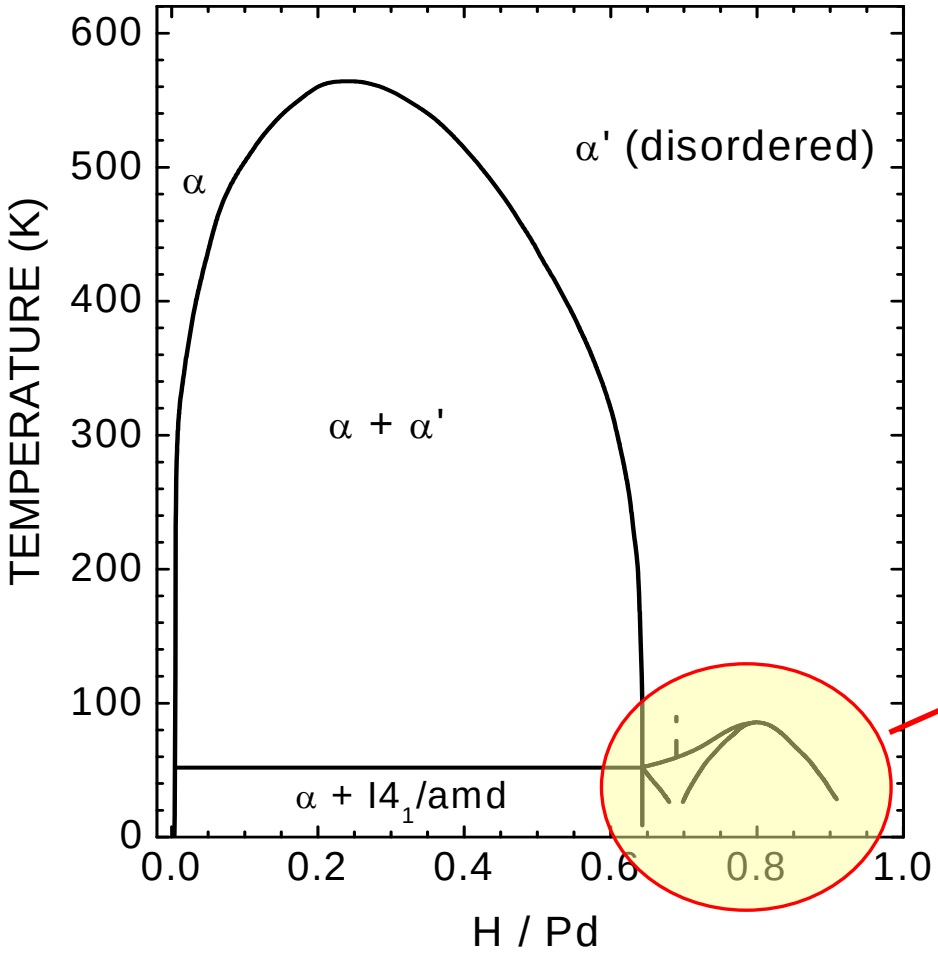
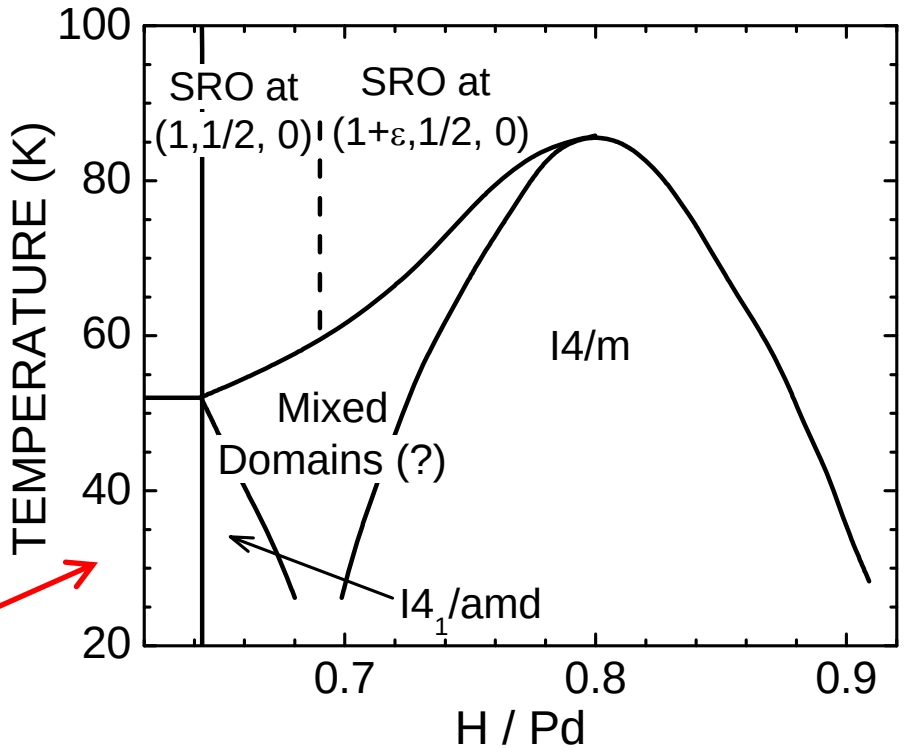
Acknowledgement: LANL Laboratory Directed Research and Development Program

Pd-H phase diagram (present understanding[1,2])



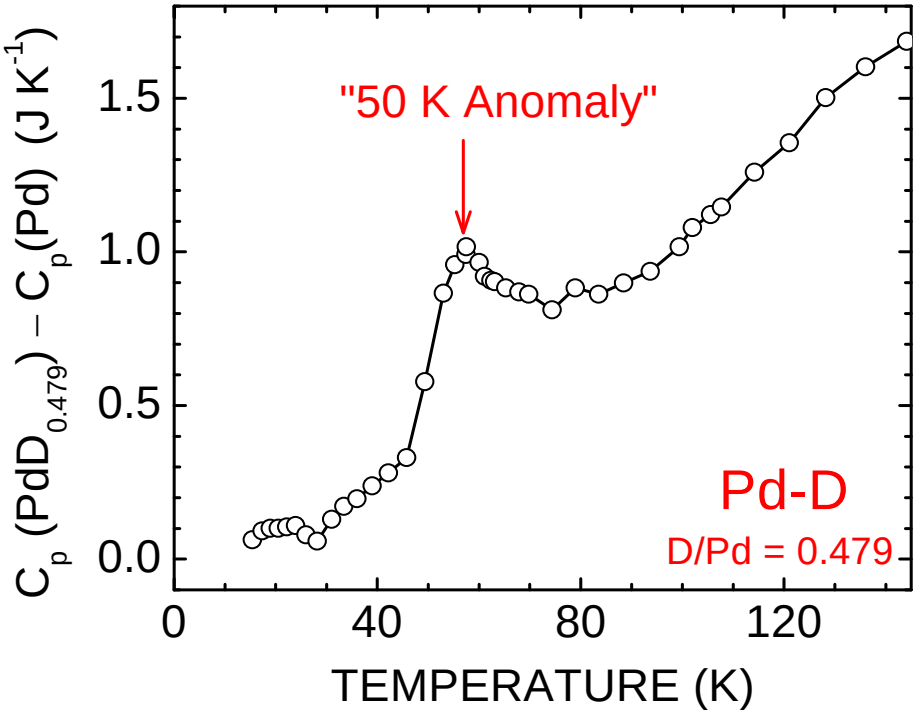


- Hydrogen-ordered structures investigated by neutron diffraction (Anderson *et al.*, 1978; Ellis *et al.*, 1979; Blaschko *et al.*, 1979-1984)

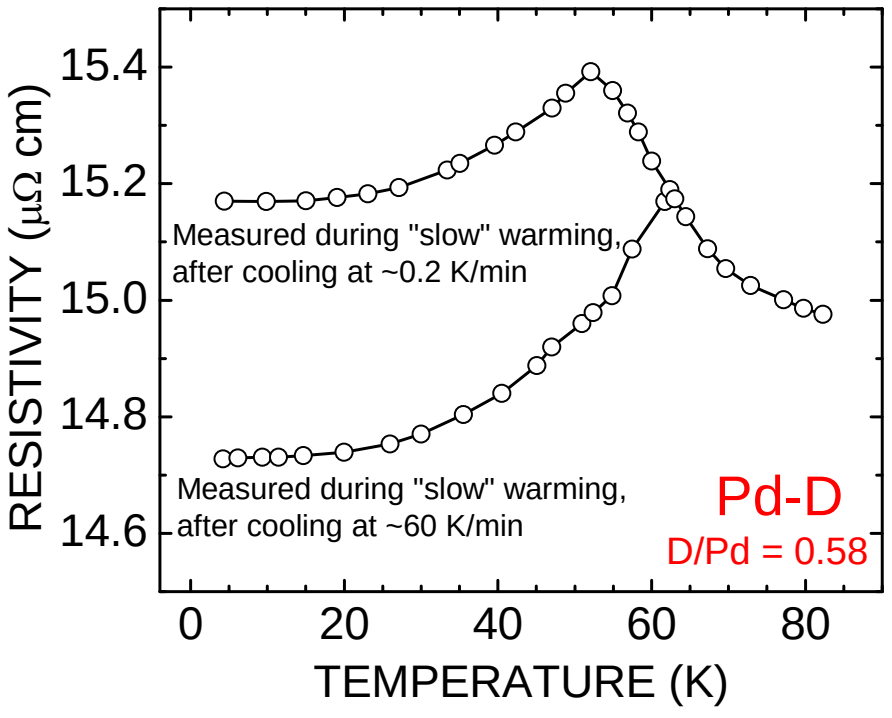
[1]T. B. Flanagan, Ann. Rev. Mater. Sci. **21** (1991) 269, [2]O. Blaschko, Phys. Rev. B **29** (1984) 5187

Signatures of H ordering in heat capacity, resistivity

Heat Capacity (Nace and Aston, 1957):



Resistivity (Ho and Manchester, 1969):



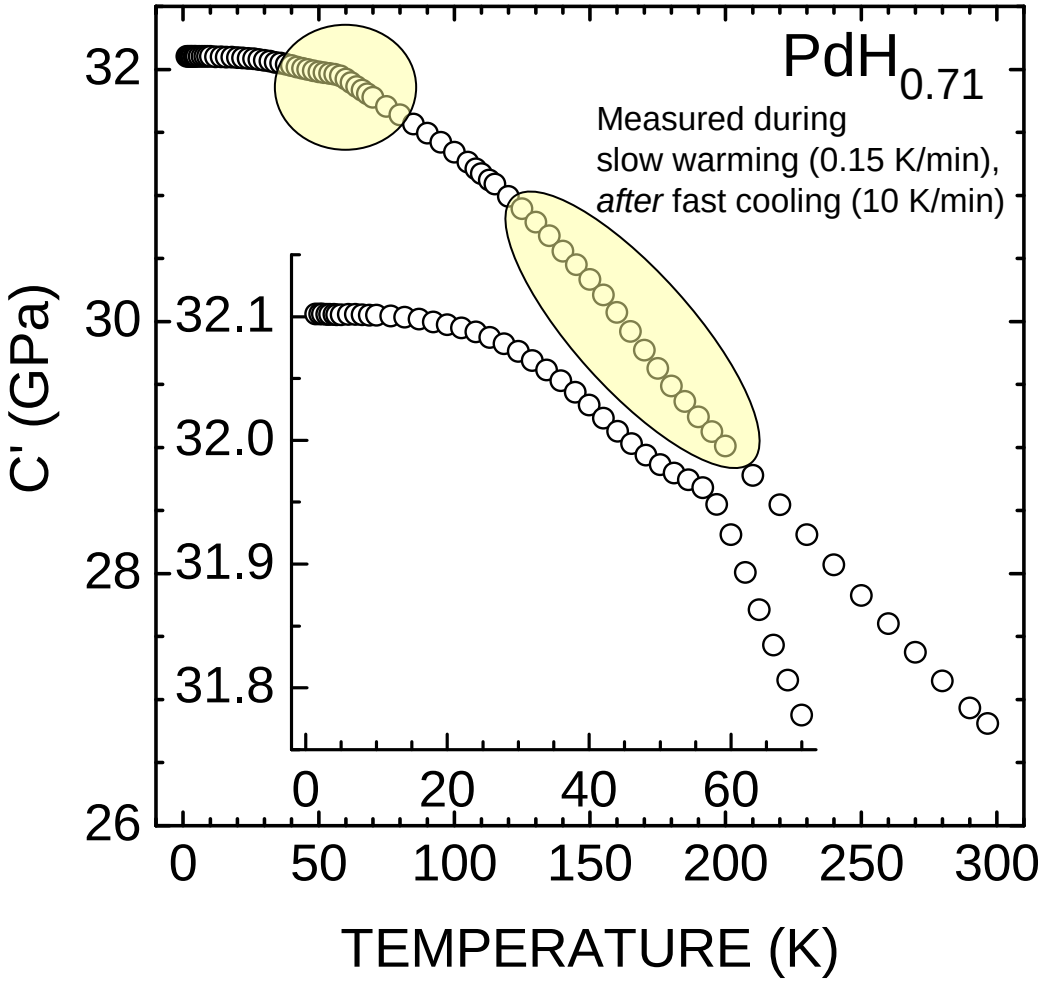
- Problems with interpreting resistivity data in terms of order-disorder *phase transition*
- Anomaly absent from elastic constant data of Hsu and Leisure (1979)

We studied H ordering in PdH_x using ultrasonic methods

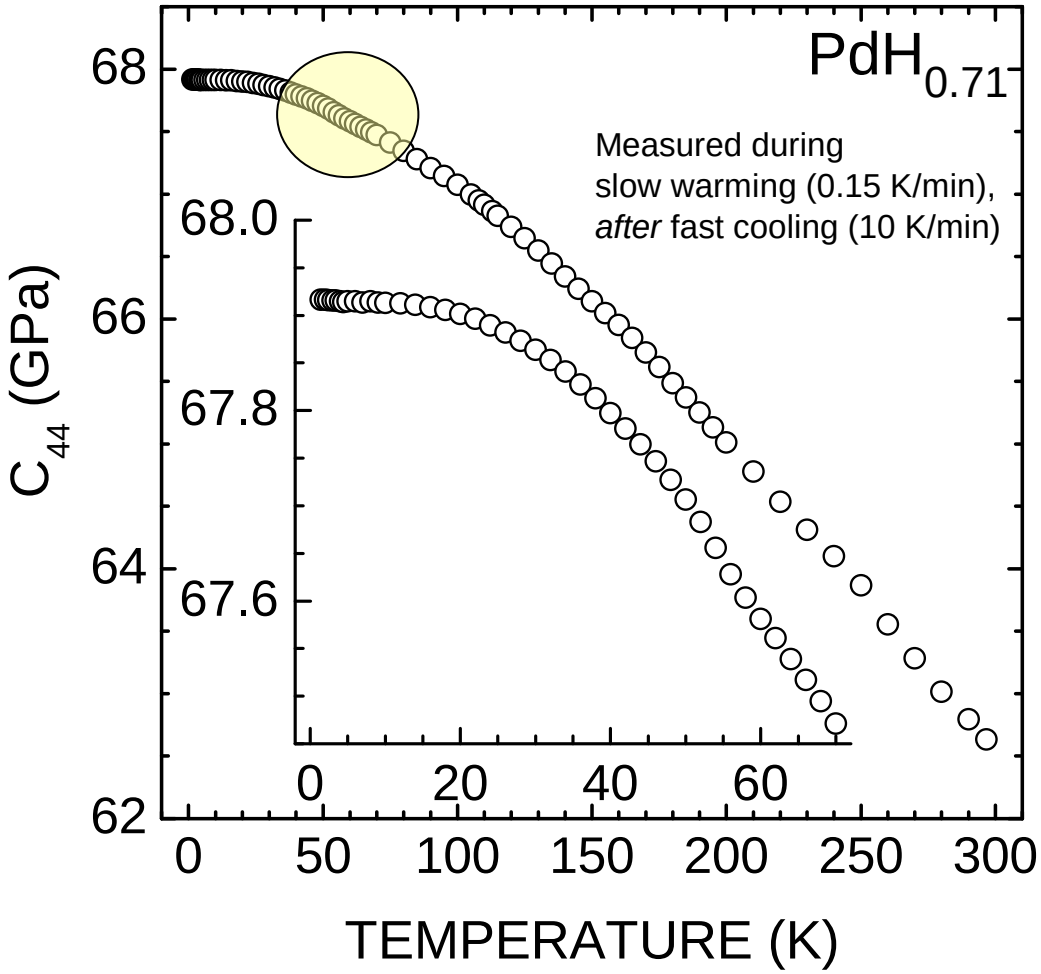
- Using Resonant Ultrasound Spectroscopy, we measured the
  - three independent elastic constants (B, C_{44}, C')
  - internal friction (acoustic loss)

  of *single crystal,* fcc PdH_x ($0.59 < x < 0.71$), in the temperature range $1.4 < T < 296$ K.

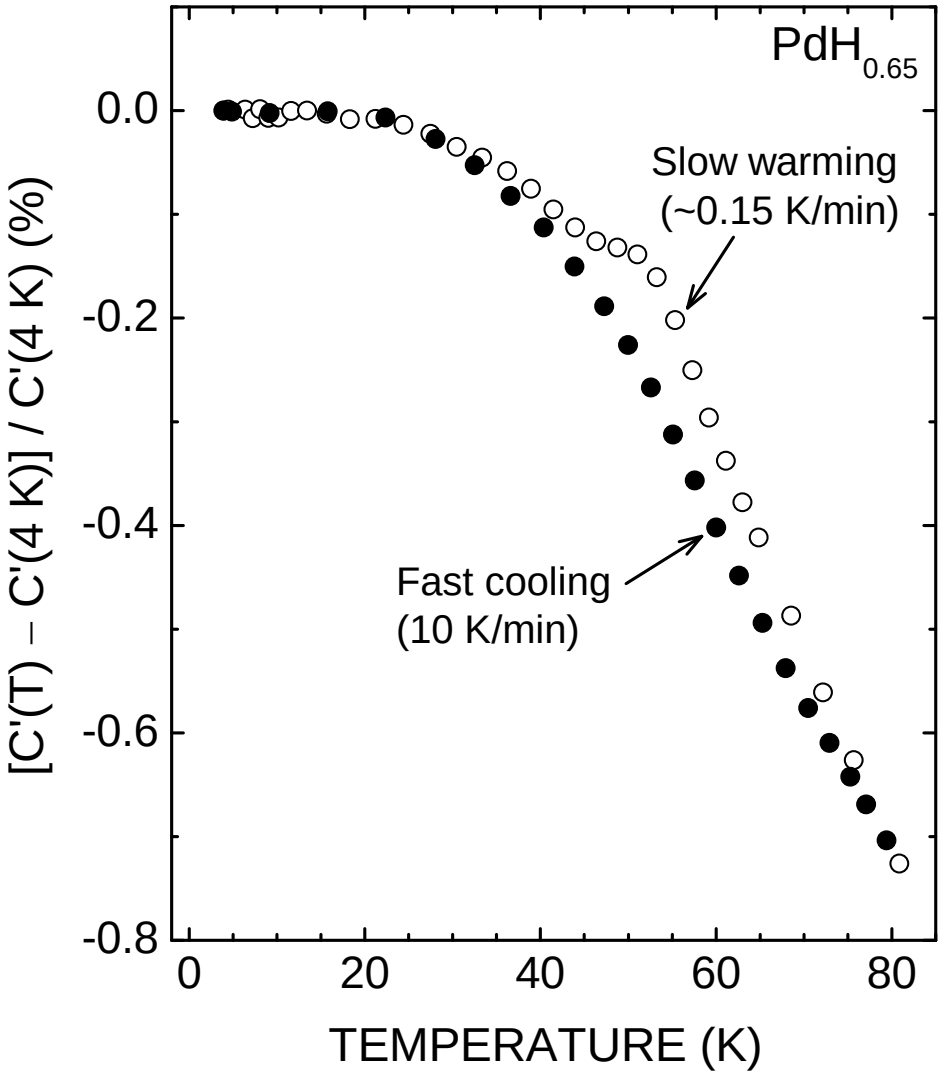
α'-phase $PdH_{0.71}$: T-dependence of C' shows two anomalies



α'-phase $PdH_{0.71}$: T-dependence of C_{44} shows one anomaly



α'-phase $PdH_{0.65}$: T-dependence of C' shows cooling/warming hysteresis



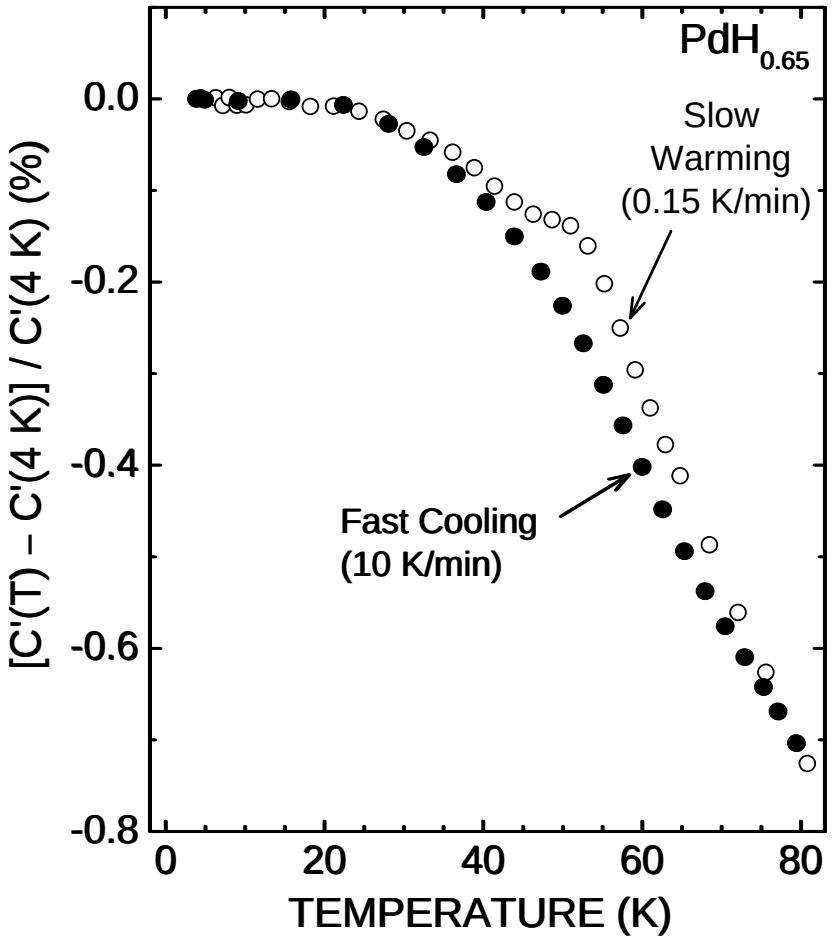
"50 K Anomaly" due to changes in hydrogen SRO

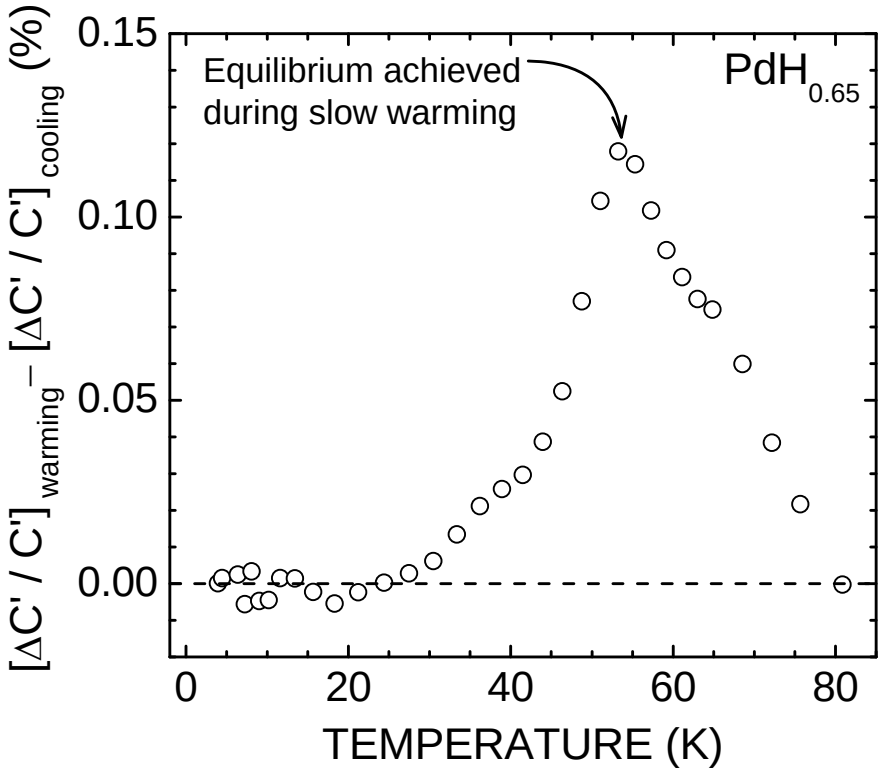
Possible explanations

- Order-disorder phase transition (*long-range* hydrogen ordering)
  - consistent with neutron diffraction measurements, but....
  - kinetics of long-range ordering *very* slow
  - cannot explain resistivity measurements

- Kinetic effect associated with changes in *short-range order* (SRO) of H atoms

"50 K Anomaly" due to changes in hydrogen SRO





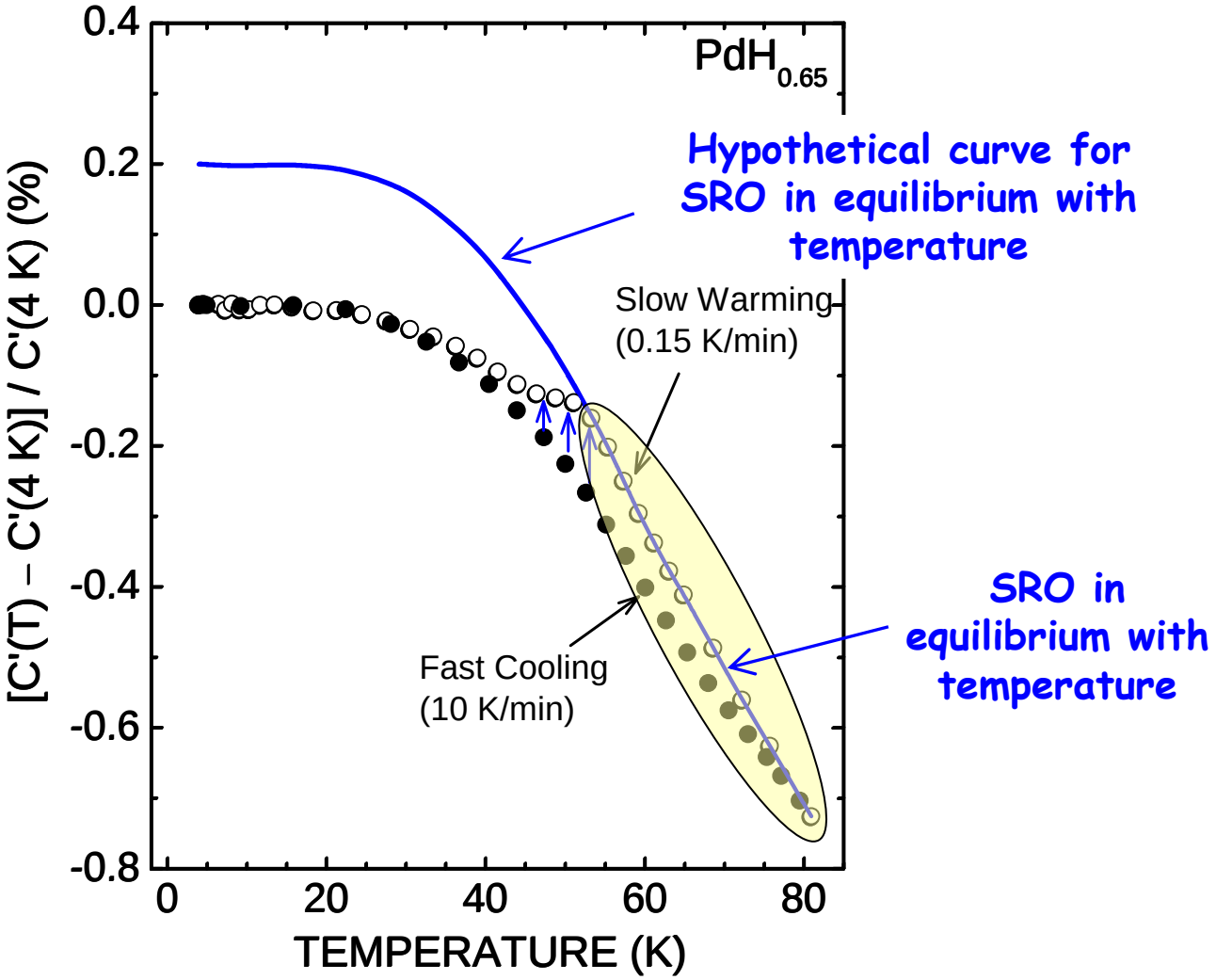
τ = 0.025 μs at 190 K [1]

τ = 7 s at 80K

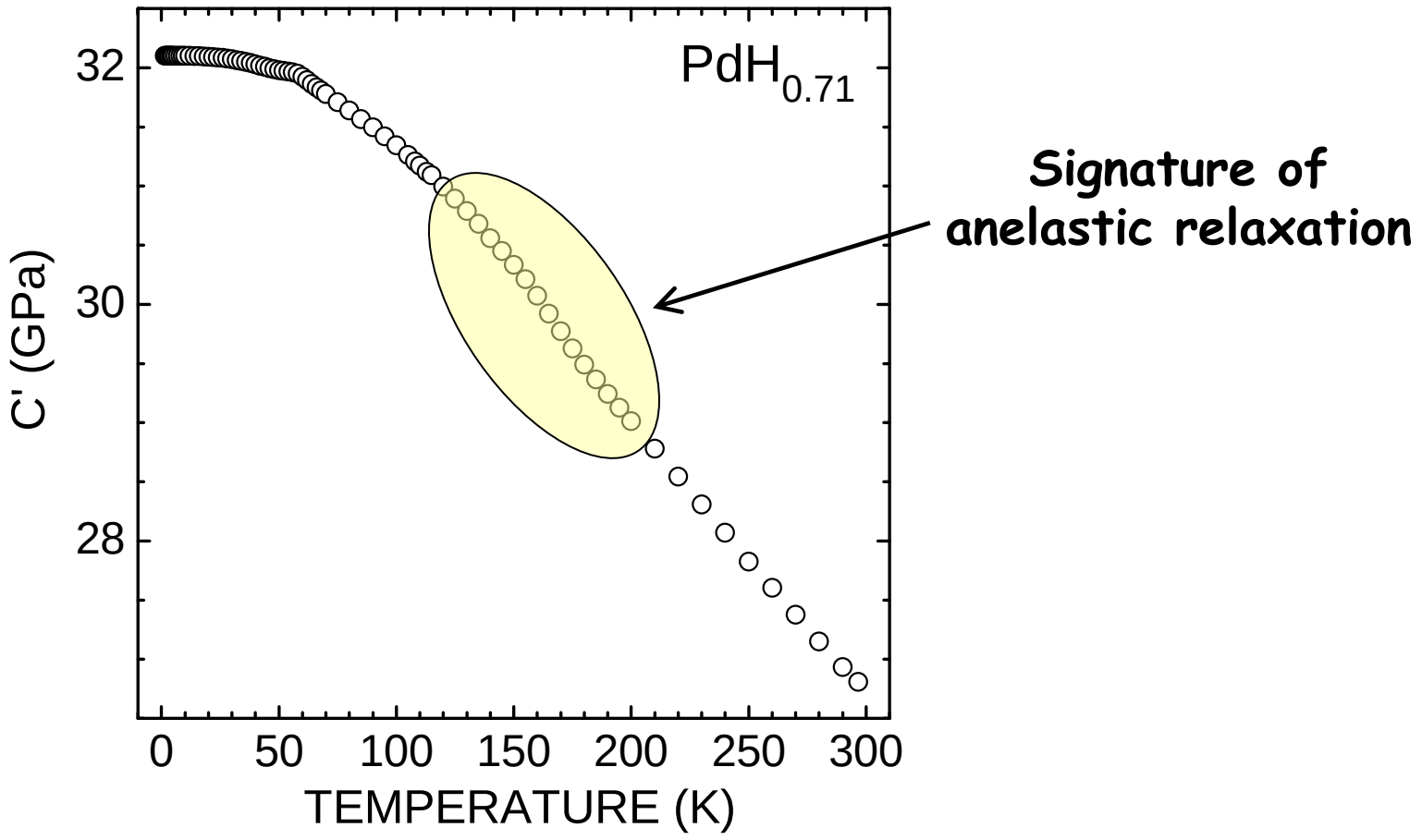
- On cooling below ~80 K, H-atom SRO is frozen at ~80 K value!

[1] R. G Leisure, L. A. Nygren, and D. K. Hsu, Phys. Rev. B **33** (1986) 8325.

"50 K Anomaly" due to changes in hydrogen SRO



Presence of SRO also explains anelastic relaxation in C'



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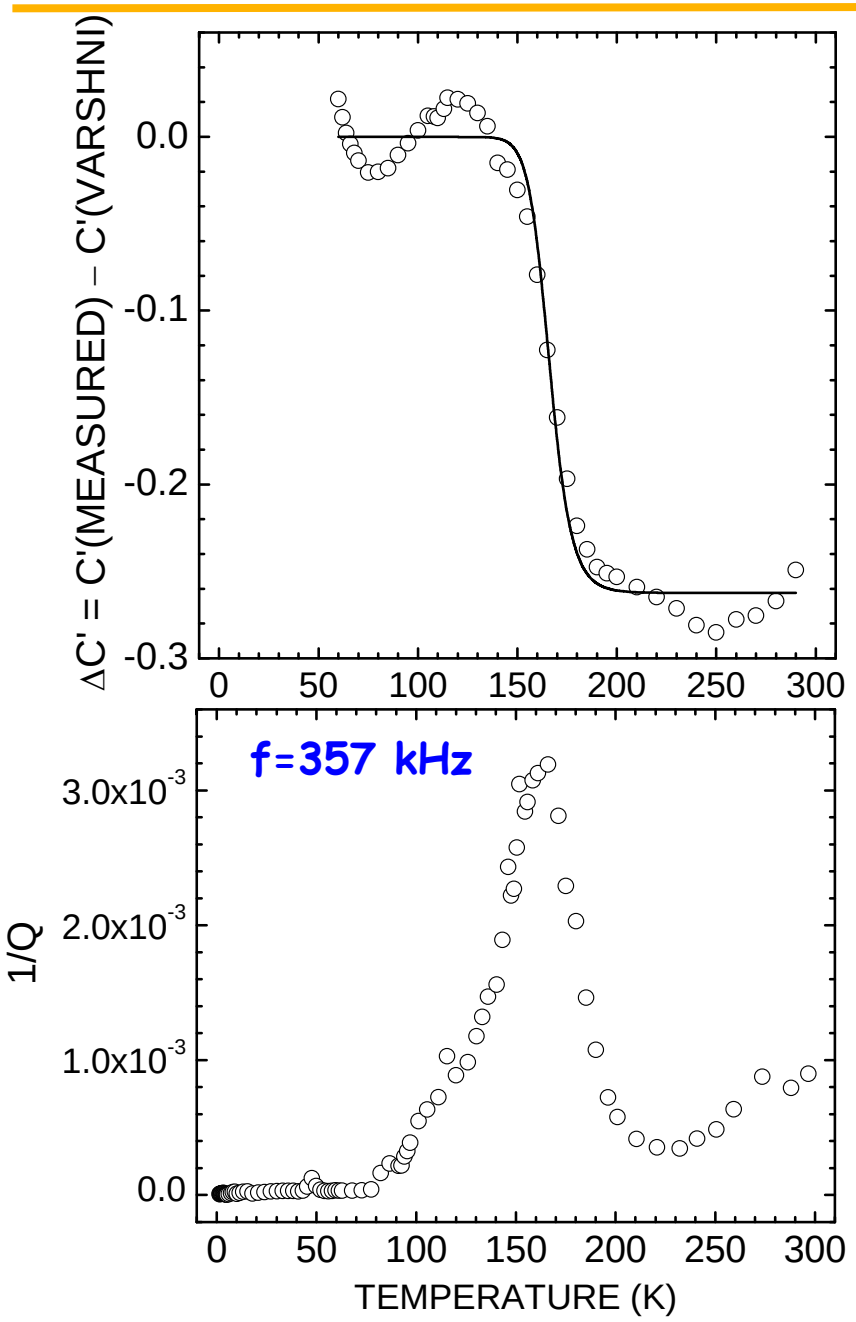
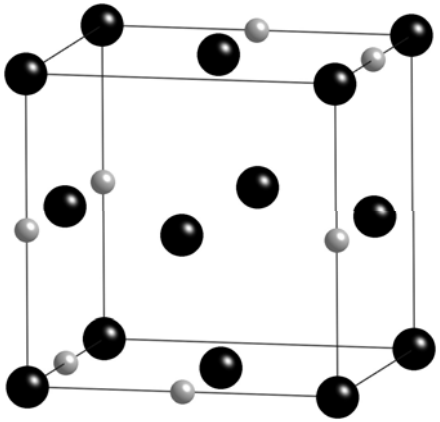


Implication:

SRO present to at least 200 K

Presence of SRO would explain anelastic relaxation in C′

- Defect must have lower symmetry than lattice sites for relaxation to occur



- H atoms occupy octahedral interstitial sites (same symmetry as fcc lattice sites)—no relaxation possible for *isolated* atoms

- Defect must consist of *cluster* of H atoms (or vacancies)—implies SRO must exist

- Presence of relaxation in C', but absence in C_{44}, implies preferential crystallographic orientation of SRO

Summary and conclusions

- We have studied H-atom SRO in PdH_x using ultrasonic techniques (RUS)
- "50 K Anomaly" is best explained as kinetic effect associated with short-range ordering of H-atoms
- Anelastic relaxation in C', in the range $120<T<200$ K, suggests that SRO persists to at least 200 K
- Presence of anelastic relaxation in C', but absence in C_{44}, implies preferential crystallographic orientation of the hydrogen SRO
- "Anomaly" at 50 K, and anelastic relaxation at ~150 K, have same physical origin (changes in SRO), but we are probing them on different time scales