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VI ALBA Users Meeting
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Structural insights into the barocaloric effect in $Fe^{II}(pap\text{-}5NO_2)_2$ spin-crossover complex.

Dra. Gloria Subías Peruga

David Gracia, Vera Cuartero, Marco Evangelisti, Javier Blasco, Emmanouil Charkiolakis, Catalin Popescu, Marie-Laure Boillot and Talal Mallah

Outline

1. **Motivation**
   - Barocaloric green refrigeration
   - Why molecular Fe^{II} spin-crossover complexes?
2. **Results**
   i. Low-pressure synchrotron powder X-ray diffraction
   ii. Calorimetry
3. **Conclusions**

Motivation – Barocaloric green refrigeration

- **Refrigeration** is **essential** for *health and comfort, conservation of food and medicines, electronics* … but it represents 30% of total electricity and it is a growing energy sector.

- Vapor-compression, the current technology:
  - ☞ HFC-based refrigerant gases → global warming
  - ☞ Limited energy effciency (40%)

To go green

SUSTAINABLE DEVELOPMENT GOALS

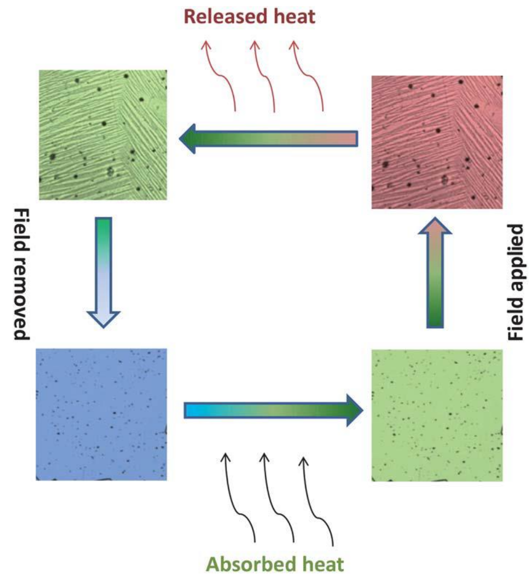
7 AFFORDABLE AND CLEAN ENERGY

13 CLIMATE ACTION

- **Solid-state caloric refrigeration**, very promising alternative:
  - ☞ Climate-friendly solid materials
  - ☞ Larger energy efficiency (60%)

Magnetocaloric (MC), elastocaloric (eC), Electrocaloric (EC), **barocaloric (BC)** effects

Barocaloric effects in the solid state, edited by P. Lloveras. IOP Publishing 2023



Pressure, stress, electric or magnetic field

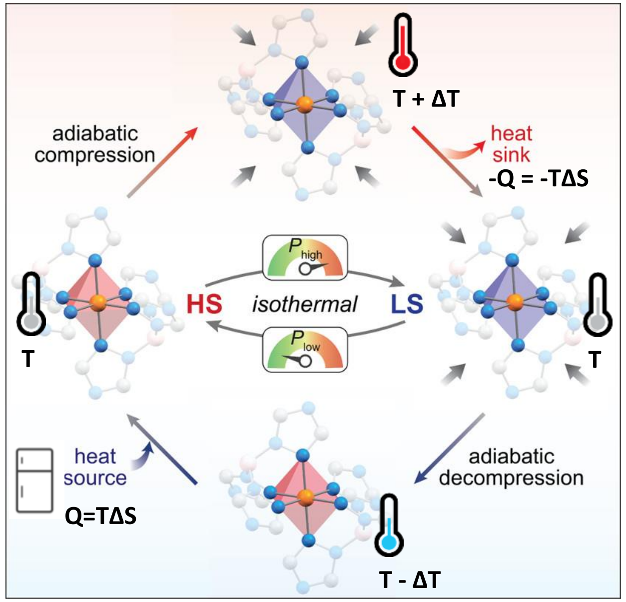
Materials showing significant changes at phase transitions in volume, strain, magnetization or polarization

L. Mañosa et al., J. Mater. Chem. A, 2013,1, 4925-4936

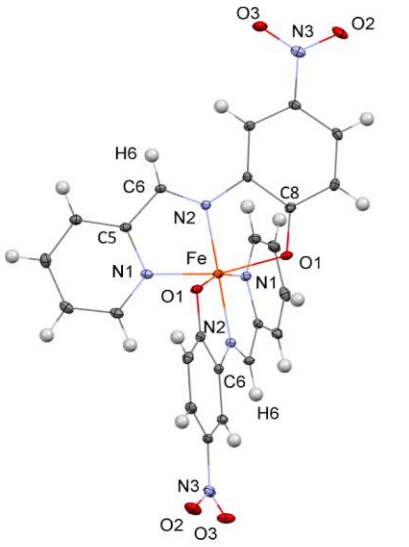
Motivation – Why molecular Fe^{II} spin-crossover complexes?

Material family	ΔS	ΔT	Reversibility	pressure	Thermal conductiv-ity	Den-sity	Cost and availability
Magnetostructural	**	*	**	*	****	****	**
Ferroelastic fluorides and oxyfluorides	**	**	***	***	**	**	****
Ferroelectrics	**	**	****	***	**	**	****
Superionic conductor	**	**	**	**	**	****	**
Hybrid organic–inorganic perovskites	**	***	****	****	*	*	**
Spin Crossovers	***	***	****	****	*	**	**
Polymers	***	***	***	*	**	*	****
Plastic crystals	****	****	**	**	**	*	****

*Poor, **Fair, ***Good, ****Excellent. P. Lloveras and J. L. Tamarit, MRS Energy & Sustainability (2021) 8:3–15



J. Am. Chem. Soc. 2022, 144, 14, 6493-6503



$Fe^{II}(pap\text{-}5NO_2)_2$
$C_{24}H_{16}FeN_6O_6$

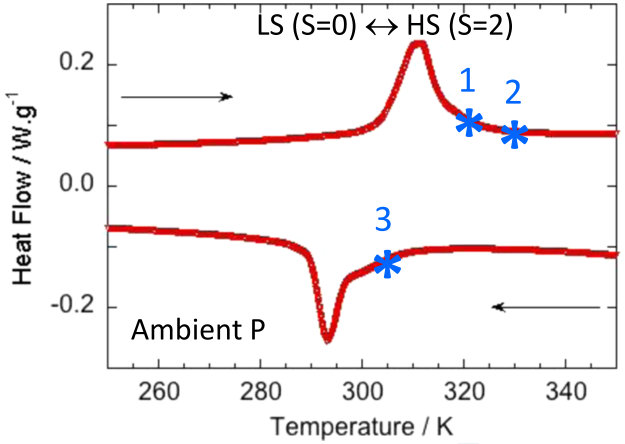
Good BC candidates:

→ large ΔH=TΔS and large ΔV
→ ΔT at low P
→ T close to RT and small hysteresis

T_t heating = 312.4 K
T_t cooloing = 296.1 K

ΔS = 30 J/mol = 55.5 J/kg K
Same C2/c monoclinic cell
Volume change ΔV/V = 4.5%

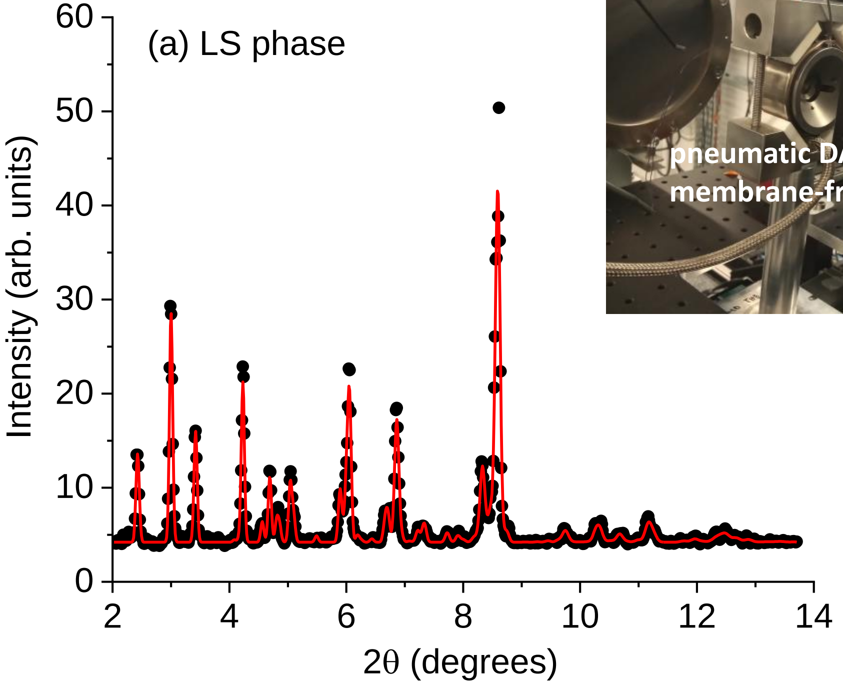
O. Iasco et al., Inorg. Chem. 2015, 54, 1791–1799

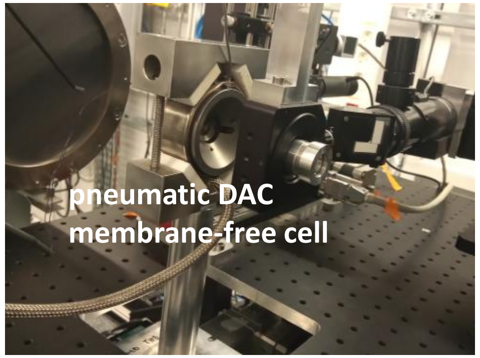


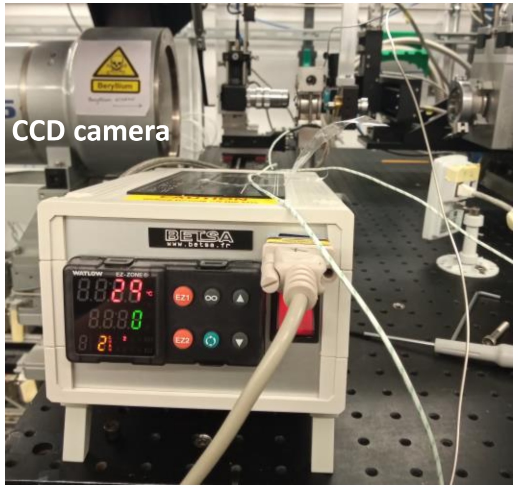
Results – Low pressure synchrotron powder X-ray diffraction

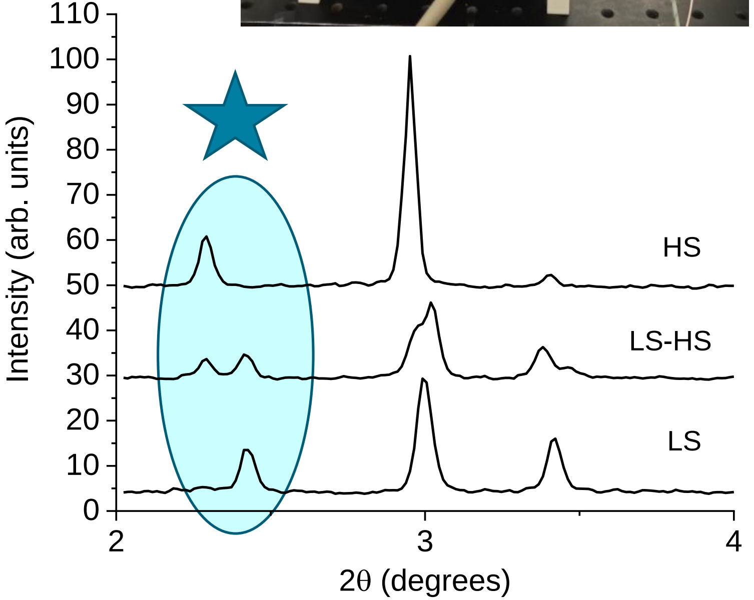
High-pressure endstation @ BL04-MSPD beamline at ALBA

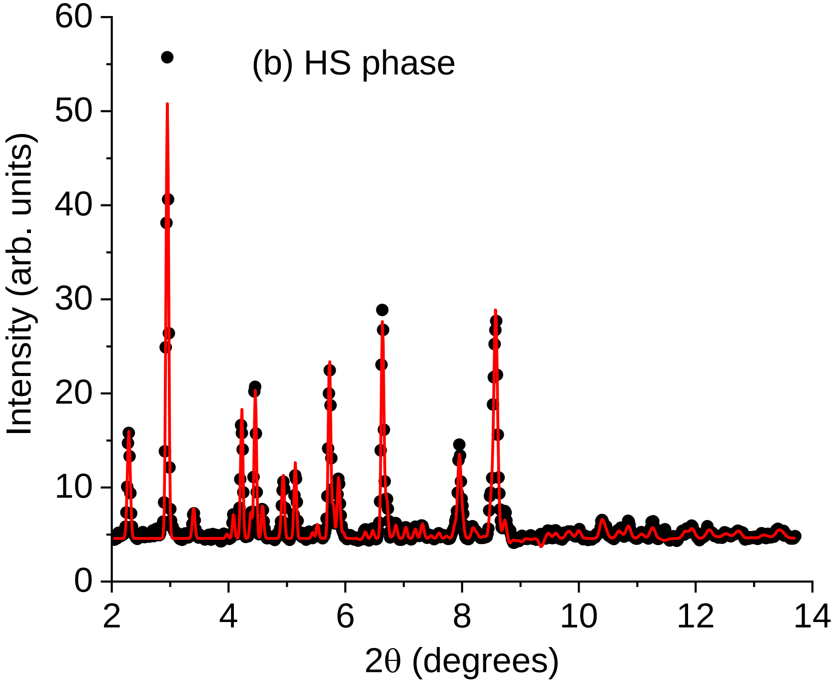
E=29.22 keV; P range: AP to 6 kbar; isothermal HPXRD patterns at T=320 K → 330 K → 310 K





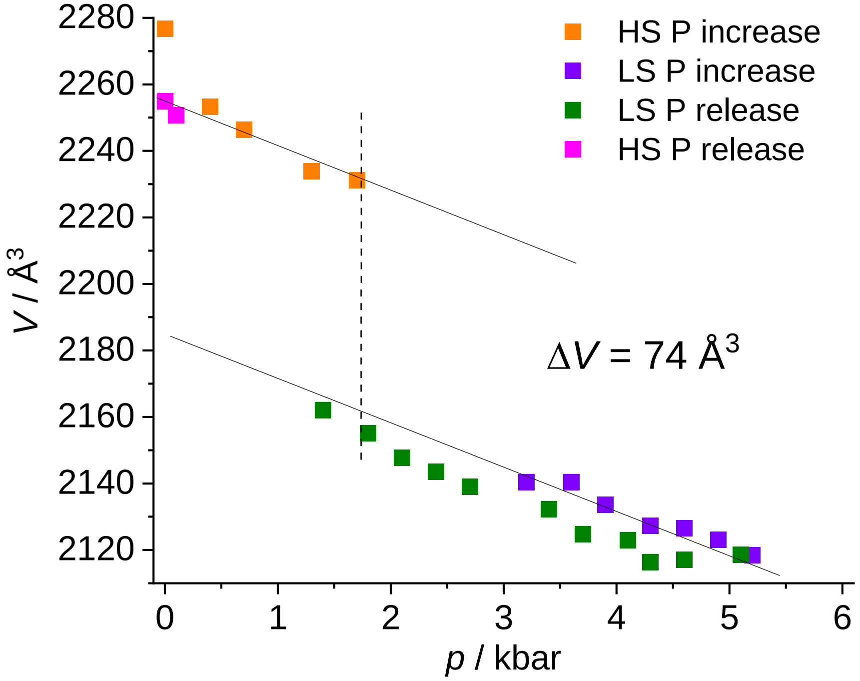


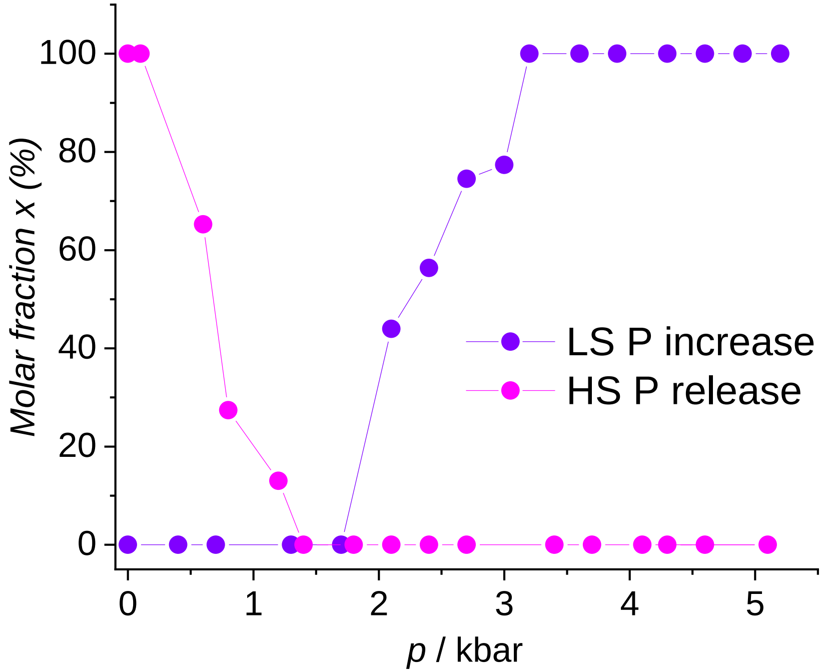




Results – Low pressure synchrotron powder X-ray diffraction

(1) T=320 K





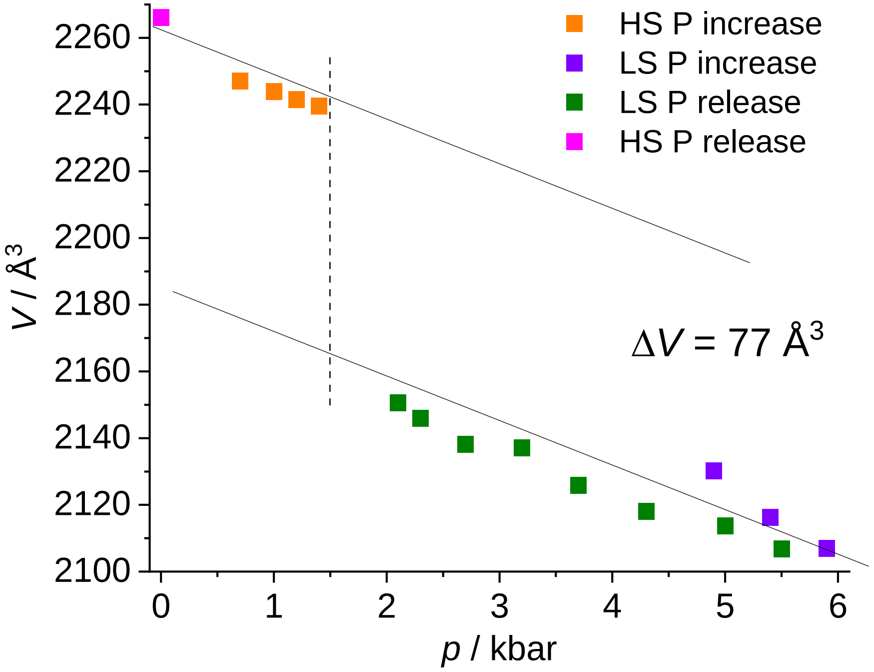
Isothermal compressibility of the LS phase:

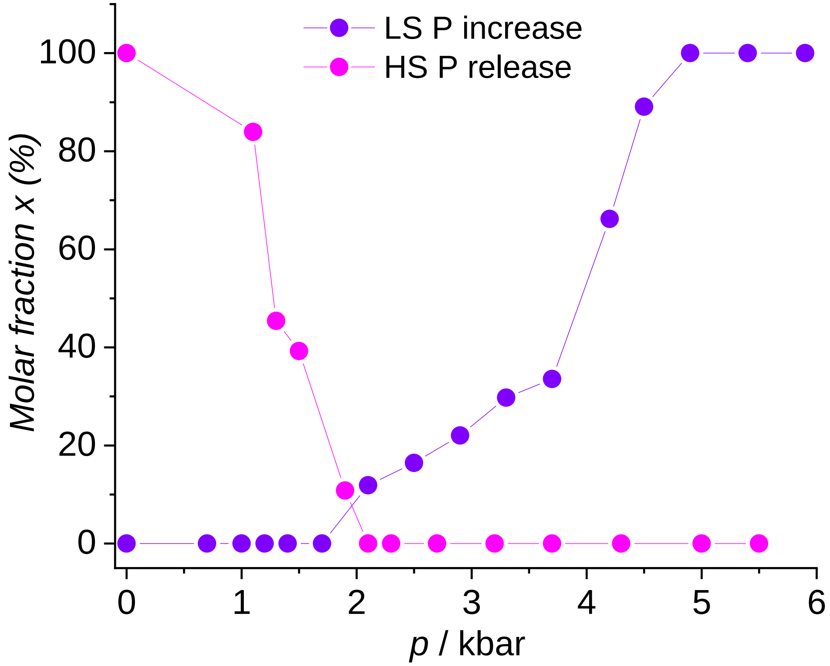
$$\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T = 0.05\ \mathrm{GPa}^{-1}$$

The LS phase starts at P=1.7 kbar on increasing P
& the HS phase is recovered at P=1.4 kbar on releasing P

Results – Low pressure synchrotron powder X-ray diffraction

(2) T=330 K





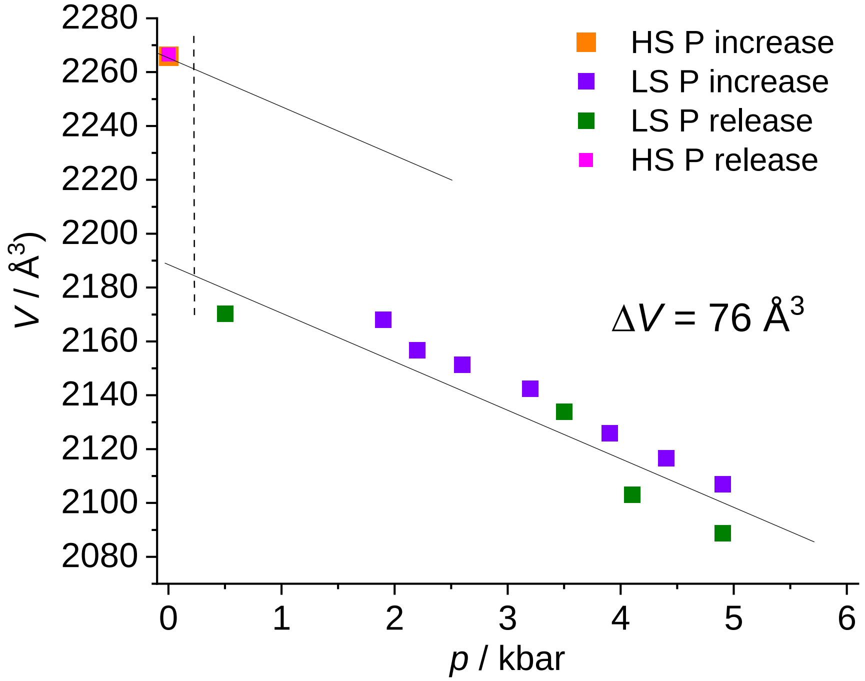
Isothermal compressibility of the LS phase:

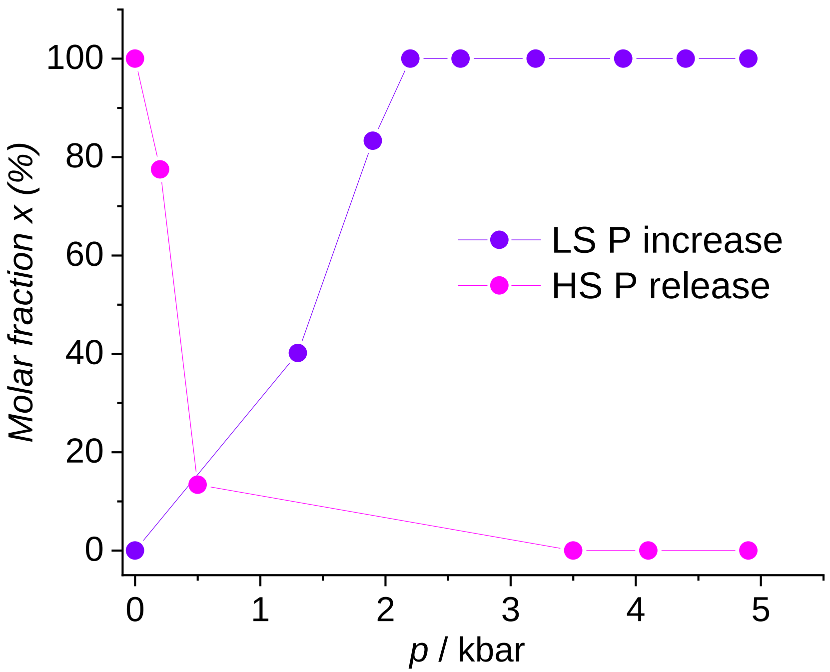
$$\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T = 0.048\ \text{GPa}^{-1}$$

The LS phase starts at P=1.7 kbar on increasing P
& the HS phase is recovered at P=1.9 kbar on releasing P

Results – Low pressure synchrotron powder X-ray diffraction

(3) T=310 K



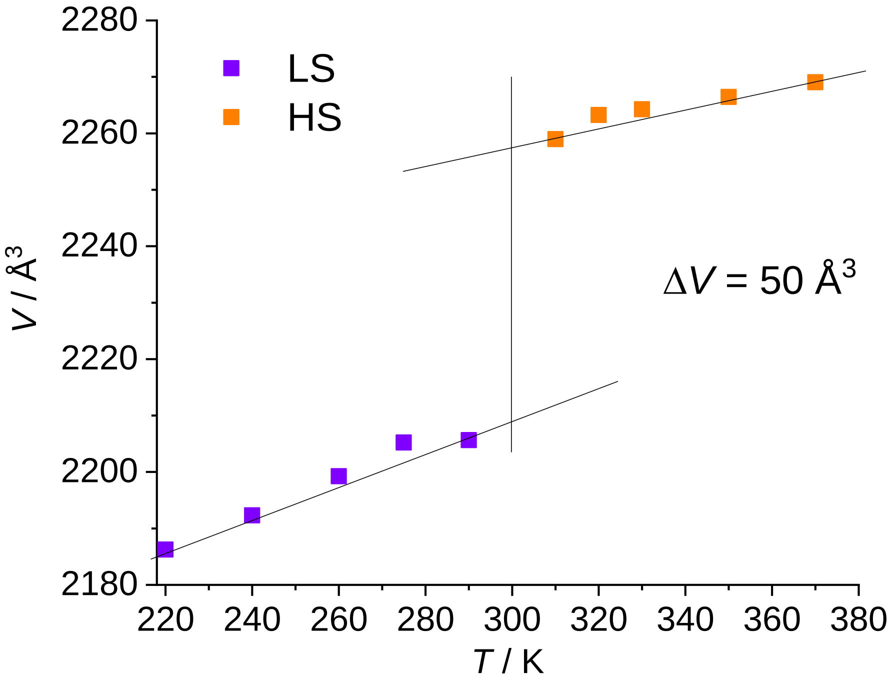


Isothermal compressibility of the LS phase:

$$\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T = 0.085\ \mathrm{GPa}^{-1}$$

The LS phase starts at ~1 kbar on increasing P
& the HS phase is recovered at 0.5 kbar on releasing P

Results – Ambient pressure X-ray diffraction



Volumetric expansion (LS): $\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p = 1.63\text{x}10^{-4}\ K^{-1}$

Volumetric expansion (HS): $\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p = 6.78\text{x}10^{-5}\ K^{-1}$

Estimation of the lattice entropy change at the transition:

$$\Delta S_v = (\beta/\kappa)\ \Delta V$$

κ average= 0.06 GPa^{-1} = $6\text{x}10^{-11}\ Pa^{-1}$.

β average = $1.1\text{x}10^{-4}\ K^{-1}$.

ΔV isothermal = 50 $Å^3$ = $1.4\text{x}10^{-5}\ m^3\ kg^{-1}$

Lattice entropy change: ΔS_V= 25.7 J $kg^{-1}\ K^{-1}$

Magnetic entropy change: ΔS_m= R ln(5)= 24.8 J $kg^{-1}\ K^{-1}$

$\Delta St = \Delta S_V + \Delta S_m$= 50.5 J $kg^{-1}\ K^{-1}$

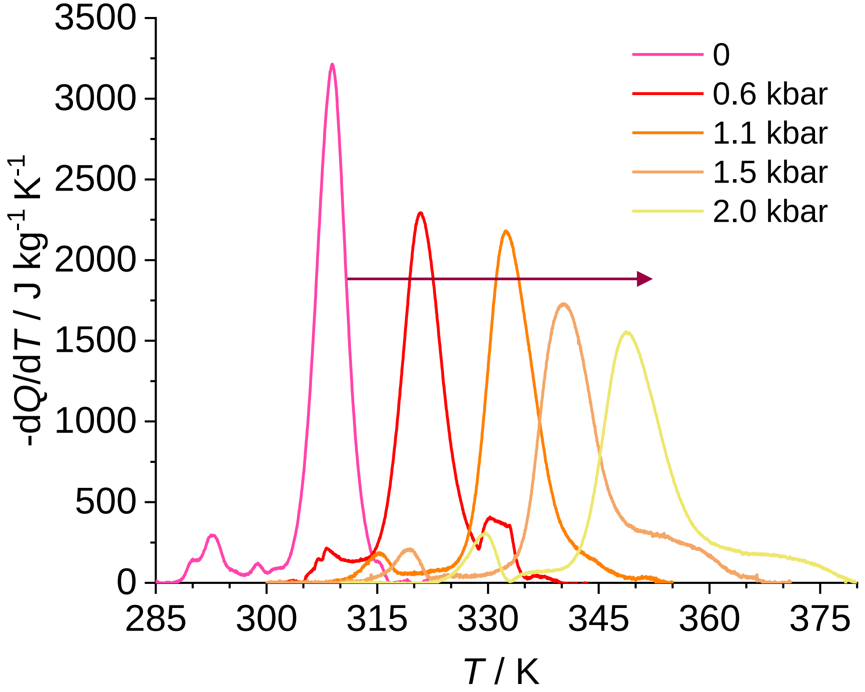
ΔSt = 55.5 J $kg^{-1}\ K^{-1}$

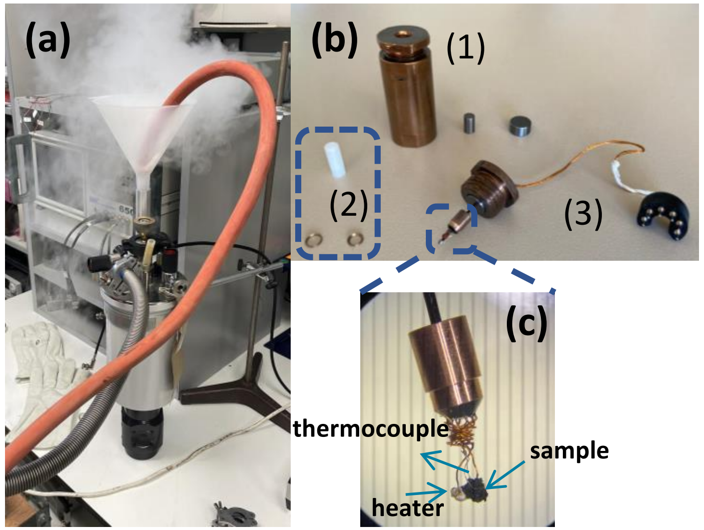
O. Iasco et al., Inorg. Chem. 2015, 54, 1791–1799

Results – Calorimetry

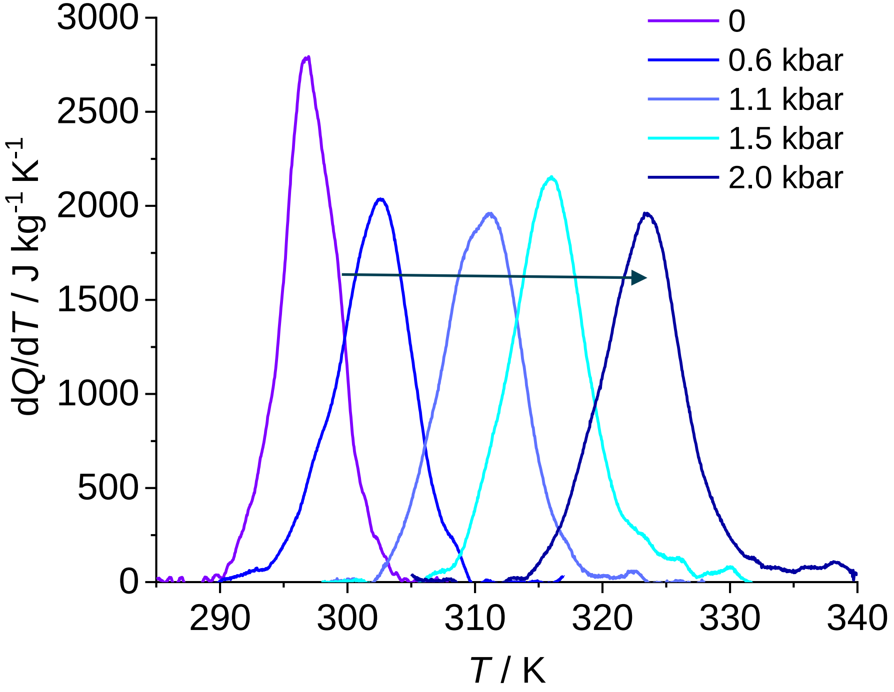
Heat capacity anomaly as a function of pressure

Heating





Cooling

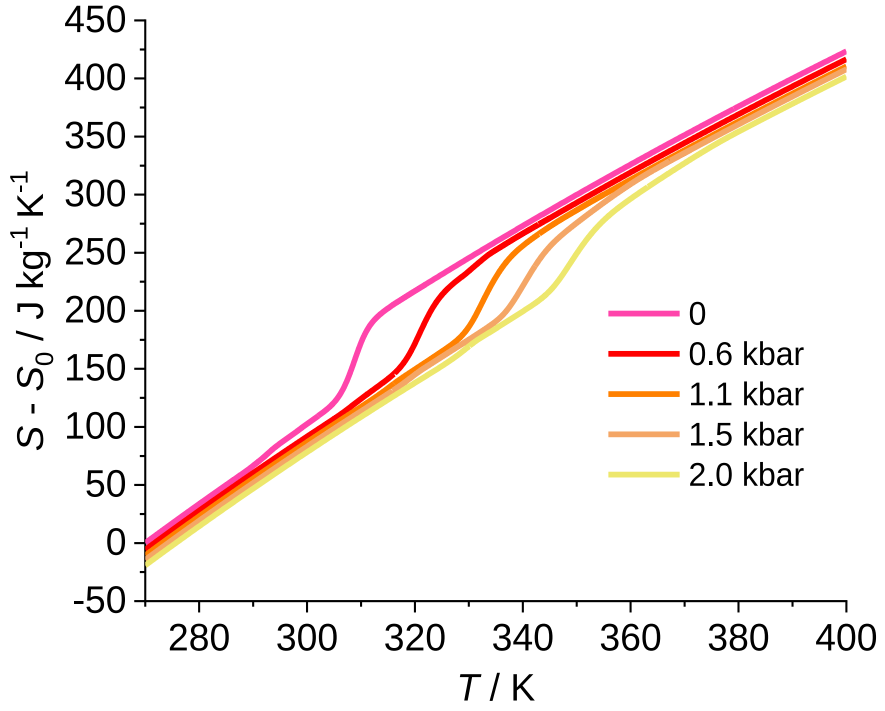


Results – Calorimetry

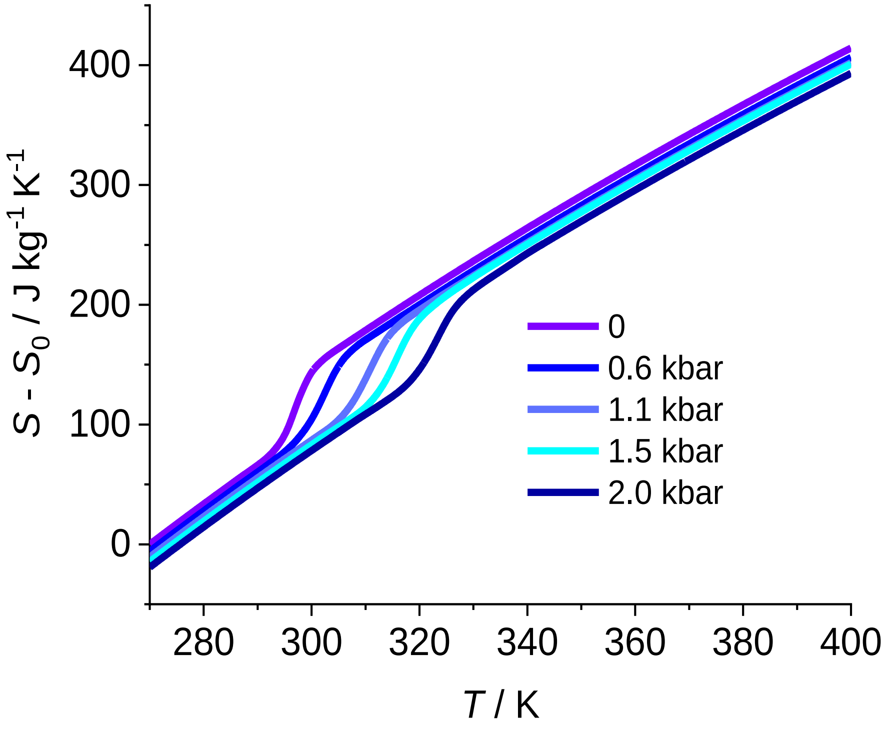
Entropy curves as a function of temperature at different P values

$$S(T,p) - S_0(T_0,p_0) = -\left(\frac{\partial V}{\partial T}\right)_{p=p_0} \Delta p + \int_{T_0}^{T} \frac{1}{T}\left(c_p + \frac{dQ}{dT}\right) dT \qquad T_0 = 270\ K$$

Heating



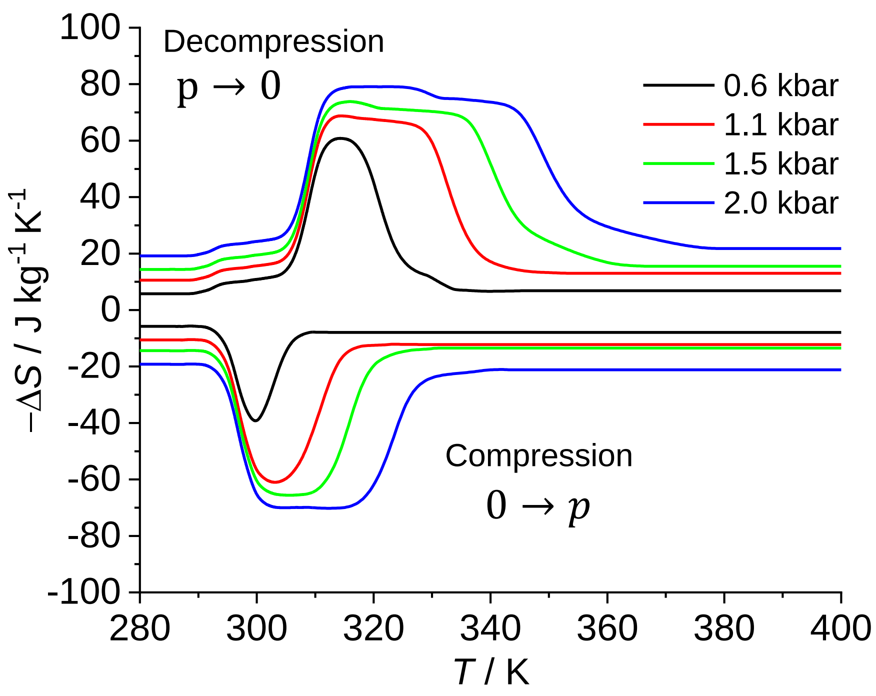
Cooling

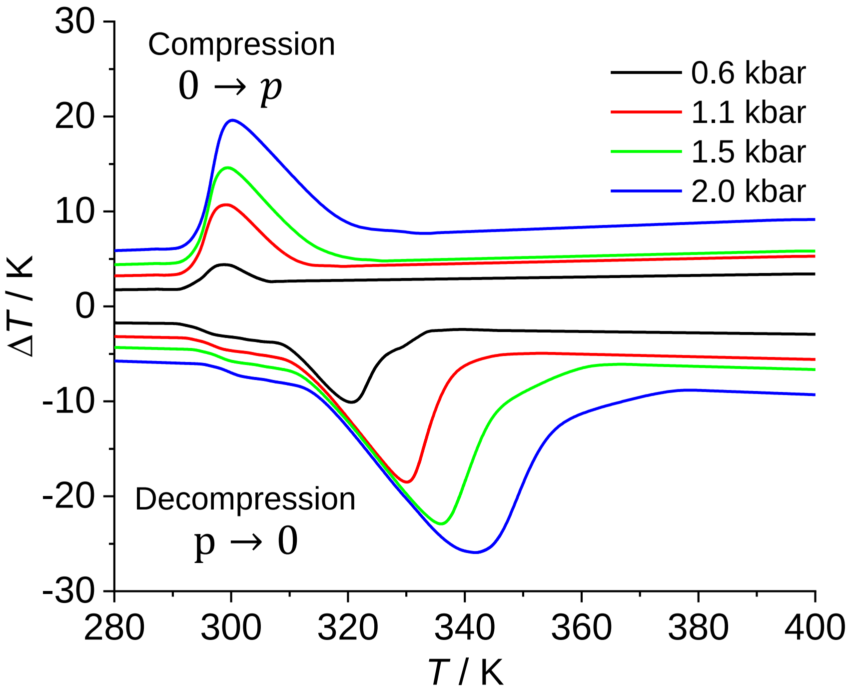


Results – Calorimetry

Isothermal Entropy change | Adiabatic Temperature change

induced by compression (cooling runs) or decompression (heating runs)



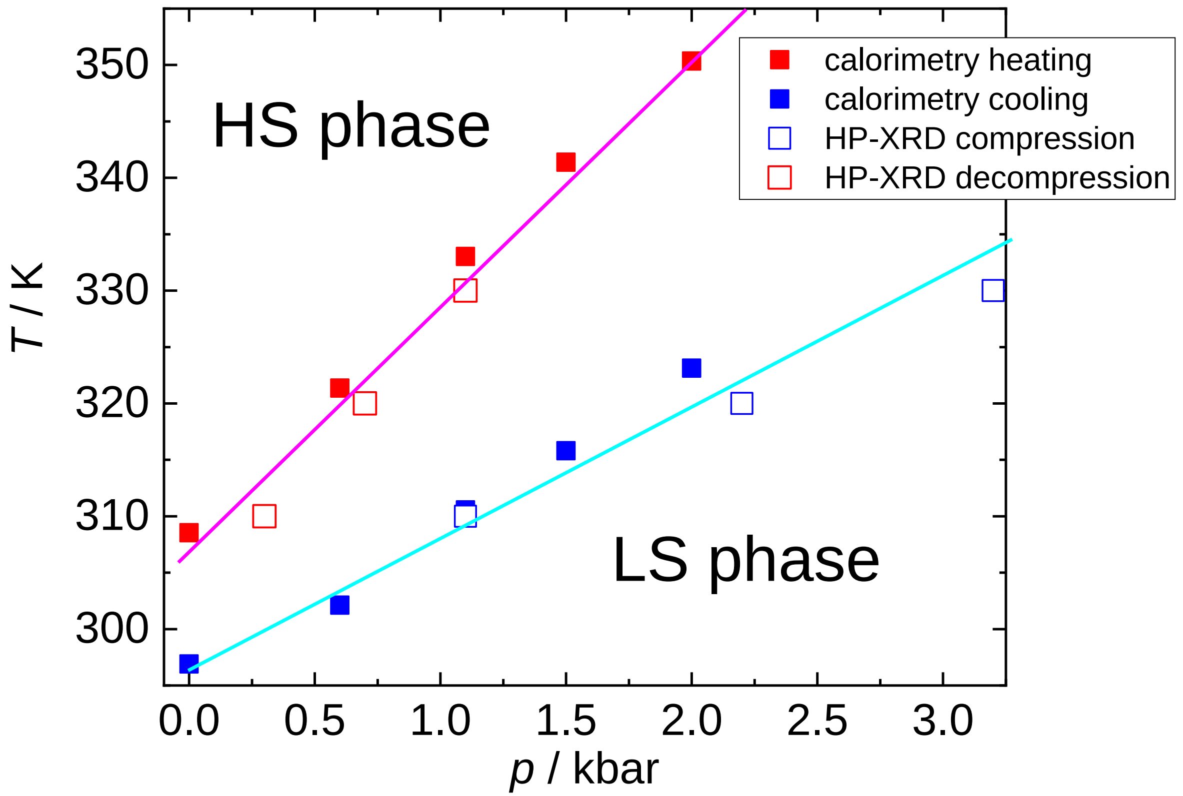


For low values of *p* (0.6 kbar), signficantly large $\Delta S \approx 50$ J Kg^{-1} K^{-1} and $\Delta T = 7$ K are found and they increase up to $\Delta S = 70$ $JKg^{-1}K^{-1}$ and $\Delta T = 20$ K for *p* =2 kbar.

Conclusions

INMA

$T - P$ phase diagram



- $Fe^{II}(pap\text{-}5NO_2)_2$ is a good candidate for BC effect as T_t spans from 297 K at ambient pressure to 330 K at 3 kbar.
- A remarkable large BC effect with ΔS =70 $JKg^{-1}K^{-1}$ and $\Delta T = 20$ K for *p* =2 kbar is reported. ✔
- Estimated transition temperature displacement with pressure:

(1) LS to HS transition
(red symbols/magenta line): dT_t/dp = 22.4 K $kbar^{-1}$
agrees with Clausius-Clapeyron equation

(2) HS to LS transition
(blue symbols/cyan line): dT_t/dp = 11.1 K $kbar^{-1}$

The hysteresis increases with pressure ✗

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Thank you for your attention!