

X-ray studies of Spincrossover Compounds in the LIEST State

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Problem:

The spin change of the molecule from LS state to HS is accompanied by an increase of the volume of the molecule and a change of its shape, which causes an increase of the volume and a deformation of the unit cell. If the molecules are considered as rigid (incompressible) the lattice parameters are expected to be proportional to the fraction of molecules in one of the spin states.

$$a_{\text{Fe}}(T) = a_{\text{Fe}}^{\text{LS}}(T) + \Delta a_{\text{HL}} \gamma_{\text{H}}(T)$$

γ_{H} : HS fraction

Since $a_{\text{Fe}}^{\text{LS}}(T)$ and $a_{\text{Fe}}^{\text{HS}}(T)$ cannot be measured in the entire temperature range, we compare the temperature variation of $a_{\text{Fe}}(T)$ with the one of $a_{\text{Zn}}(T)$.

Solution :

Assumption: The difference between the lattice constants exhibits Debye behaviour:

$$a_{\text{Fe}}^{\text{LS}}(T) - a_{\text{Zn}}(T) = \alpha_{\text{LS}} + \beta_{\text{LS}} T \quad (2)$$

$$a_{\text{Fe}}^{\text{HS}}(T) - a_{\text{Zn}}(T) = \alpha_{\text{HS}} + \beta_{\text{HS}} T \quad (3)$$

Evaluation :

$$\text{a) } a_{\text{Fe}}^{\text{HS}}(T < 50\text{K}) \text{ from LIEST state} \Rightarrow \alpha_{\text{HS}}, \beta_{\text{HS}} \text{ (fit parameters)}$$

$$a_{\text{Fe}}^{\text{HS}}(T > 230\text{K}) \text{ from thermally populated HS state}$$

$$\text{b) } a_{\text{Fe}}(T) - a_{\text{Zn}}(T) = \alpha_{\text{LS}} + \beta_{\text{LS}} T + (\alpha_{\text{HS}} - \alpha_{\text{LS}} + (\beta_{\text{HS}} - \beta_{\text{LS}}) T) \gamma_{\text{H}}(T) \Rightarrow \alpha_{\text{LS}}, \beta_{\text{LS}} \text{ (fit parameters)}$$

Experimental Setup :

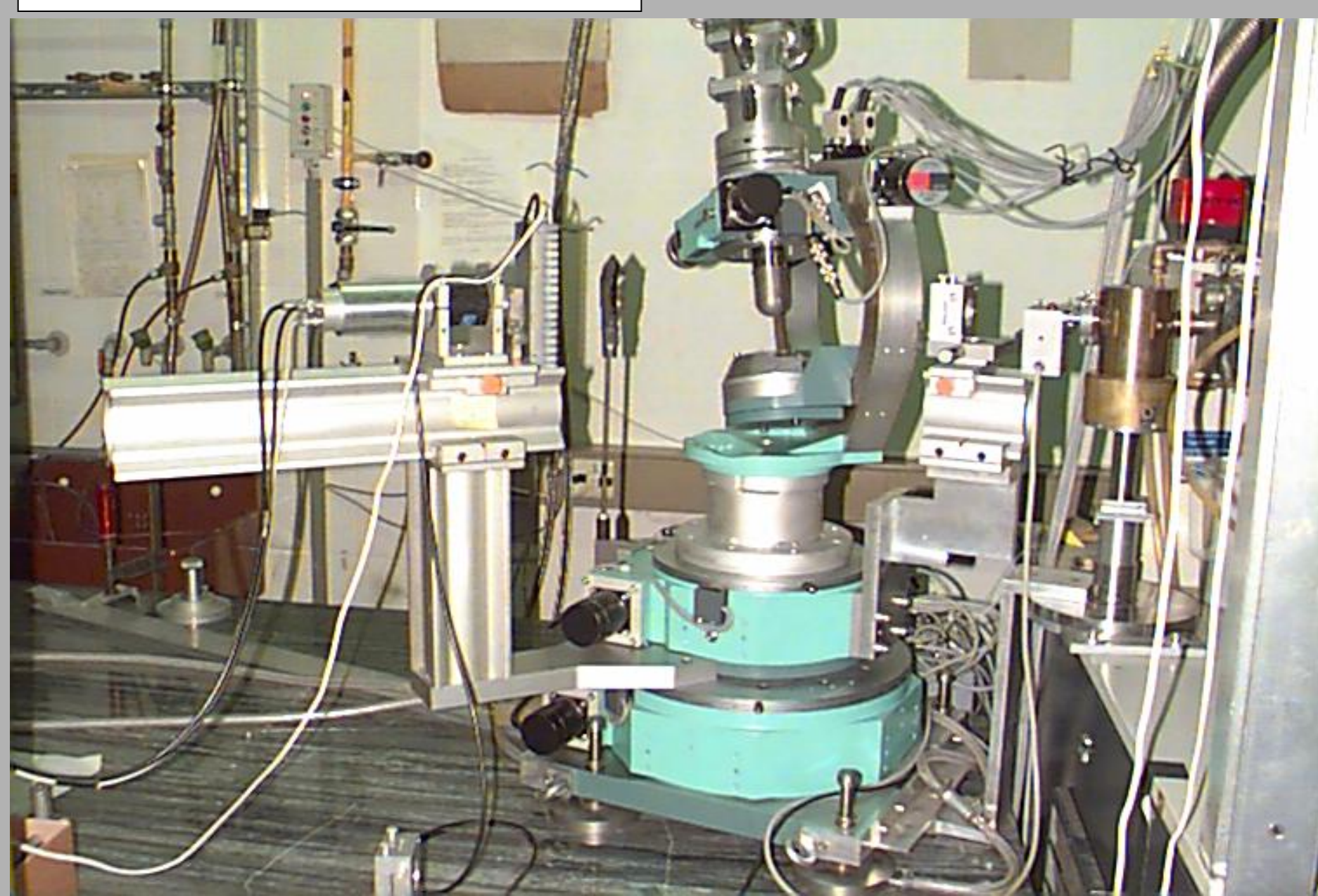
4-circle HUBER diffractometer

NONIUS rotating anode

Graphite monochromator (bent in one direction): MoK α

CRYOGENICS closed cycle He-cryostat

The 4-circle LT-diffractometer



Diffraction Geometry

Experimental Method:

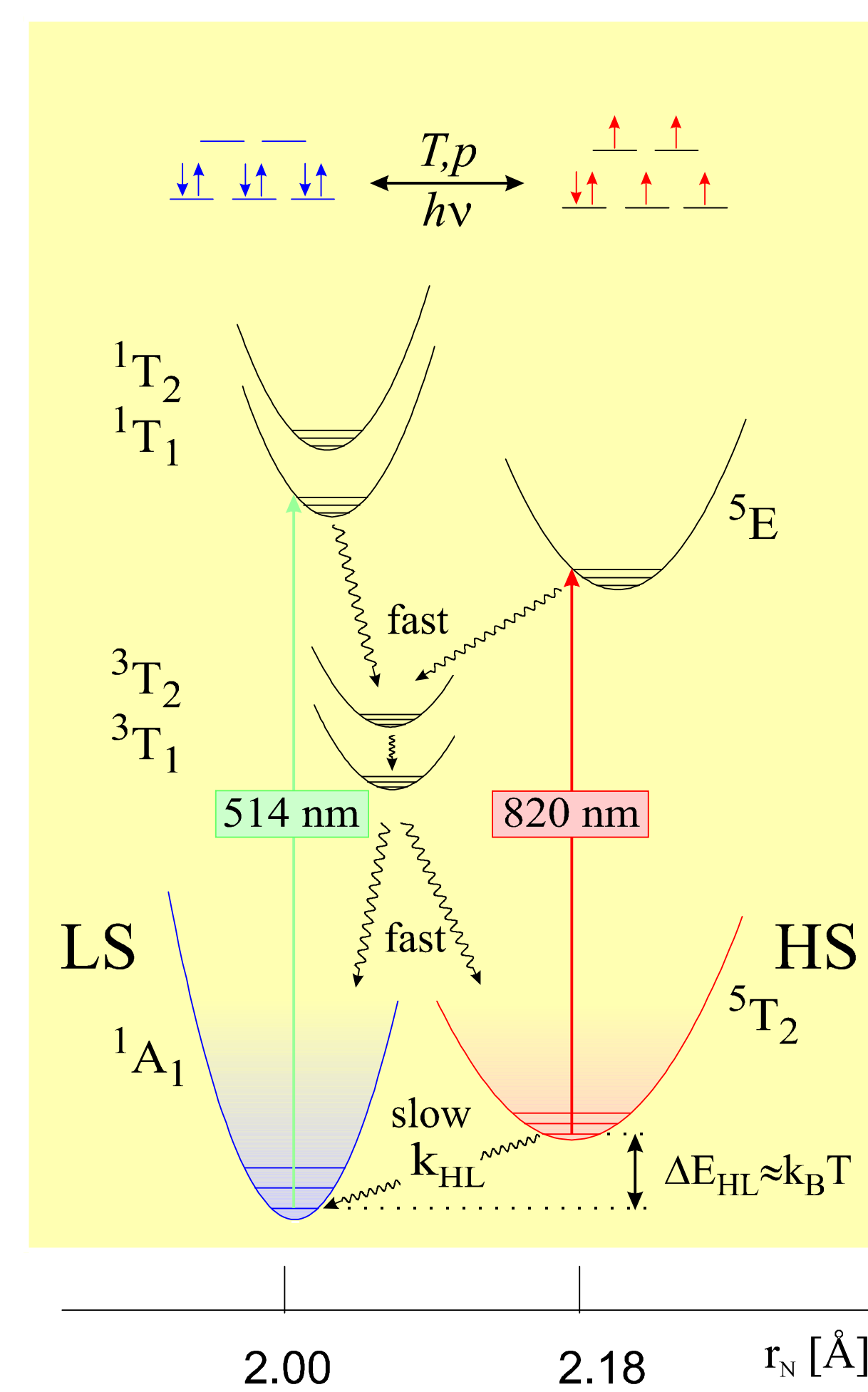
The single crystals were obtained after recrystallization of pure $[\text{M}(\text{ptz})_6](\text{BF}_4)_2$ (M=Fe,Zn; ptz=1-propyltetrazole) from a nitromethane solution. The temperature during the diffraction experiment was controlled within 0.1K. The refinement of the cell parameters was carried out by measuring of about 60 reflections with high 2θ -values and their Friedel pairs at both sides of the primary beam. An ω -scan was carried out at $+$ and -2θ and ω . The center of gravity was determined by the difference of the two ω -centers.

Experimental results:

The variation of the lattice parameters with temperature and after LIEST

LIEST

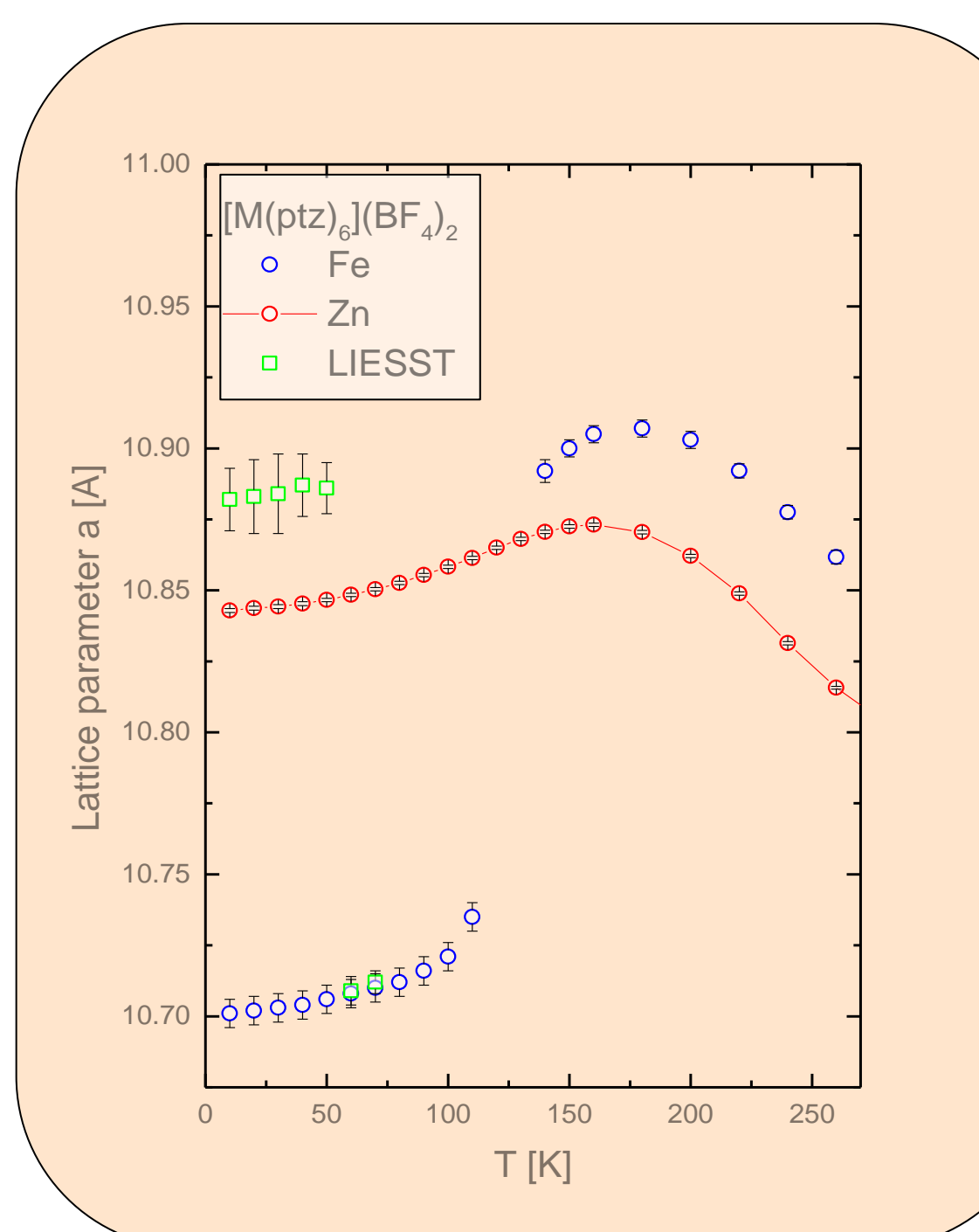
(Light Induced Excited Spin State Trapping)



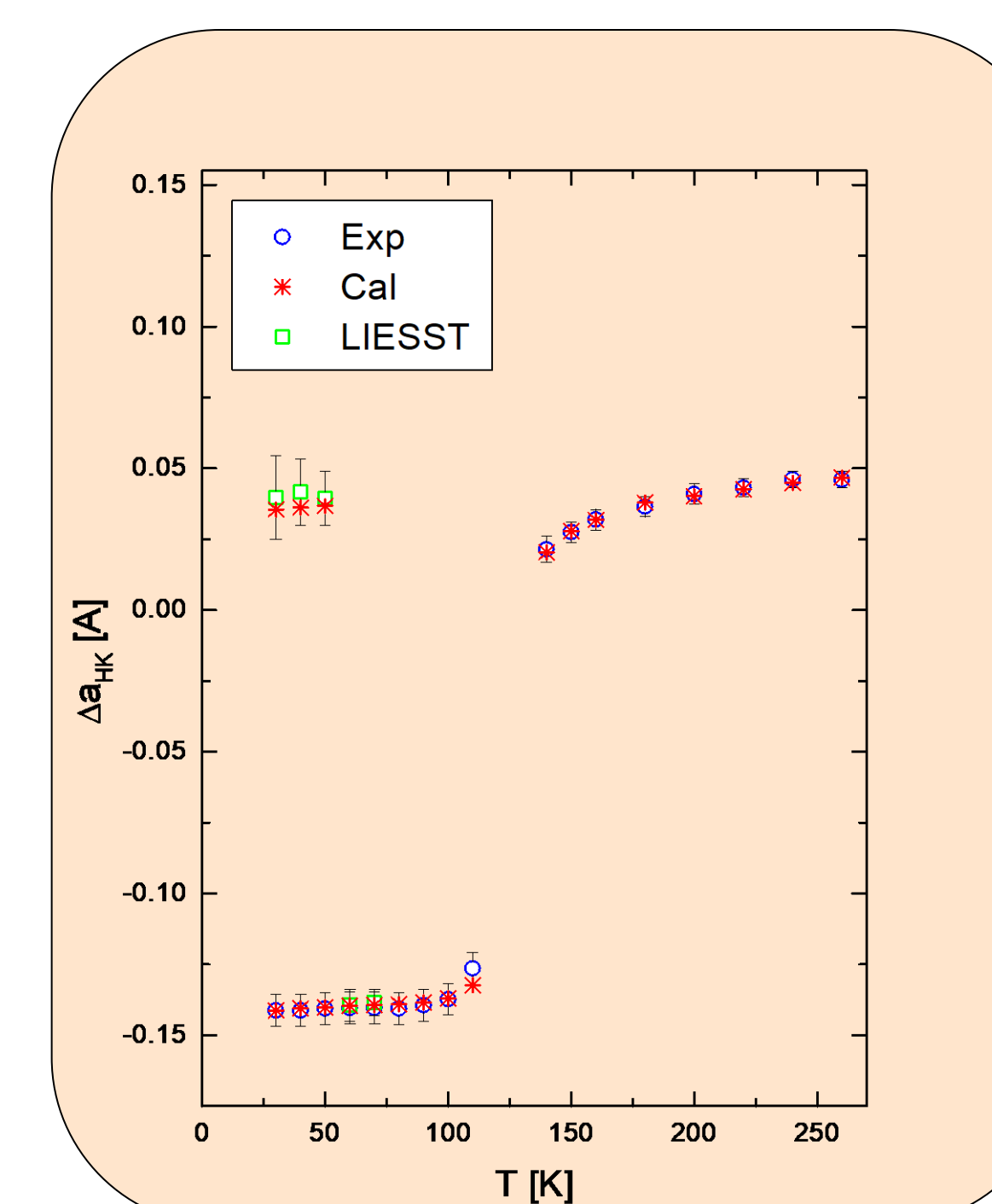
The green light from an Argon laser (514 nm) is guided by a glass fiber into the cryostat onto the crystal. The following pictures show the change of the lattice parameters after LIEST

Results :
Within the experimental error Δa_{HL} and Δc_{HL} are independent of temperature.
The spin crossover molecule behaves as incompressible

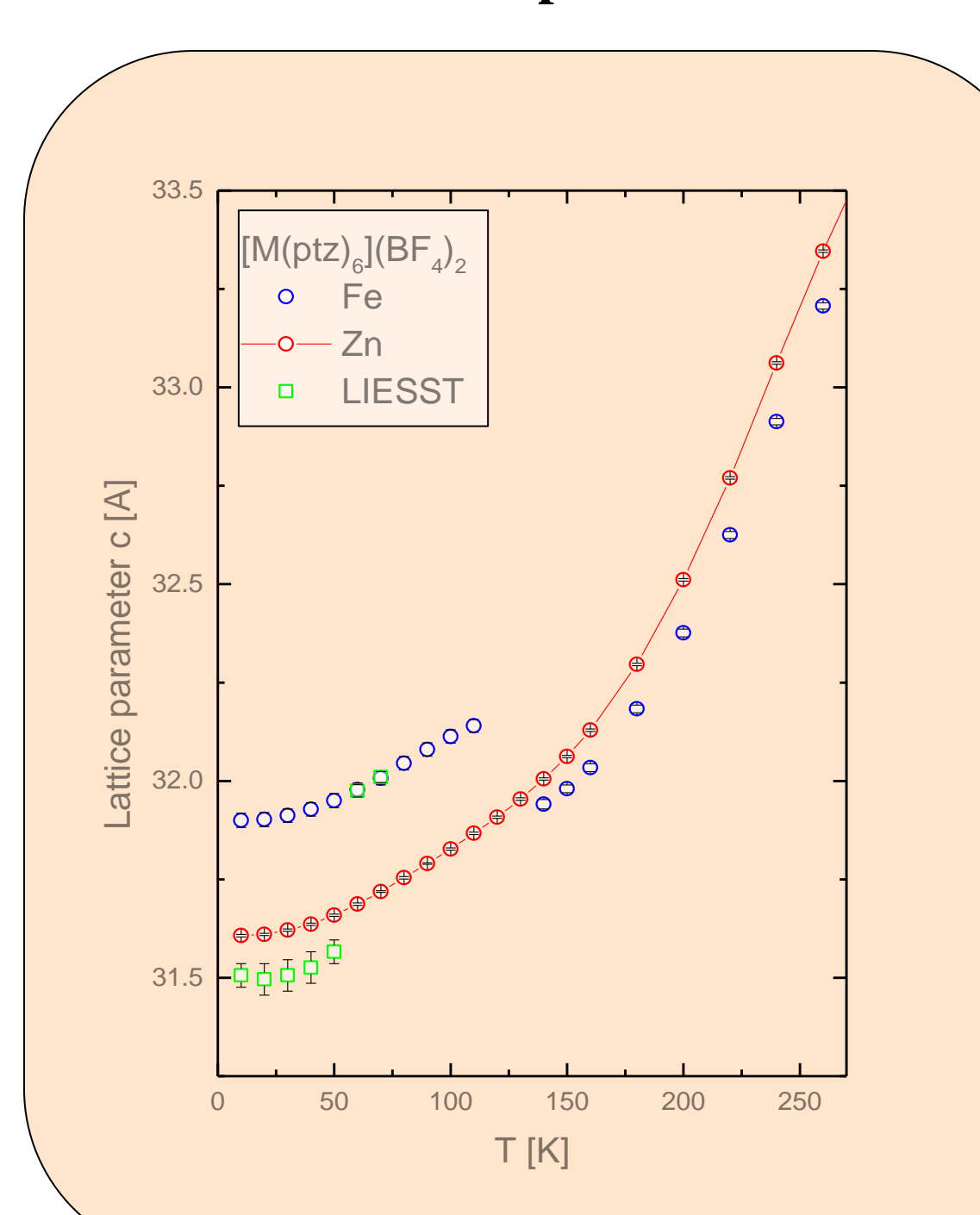
Lattice parameter a



Difference of the lattice parameter a between the iron and the zinc compound



Lattice parameter c



Difference of the lattice parameter c between the iron and the zinc compound

