Influence of charge transfer in 3d perovskite oxides

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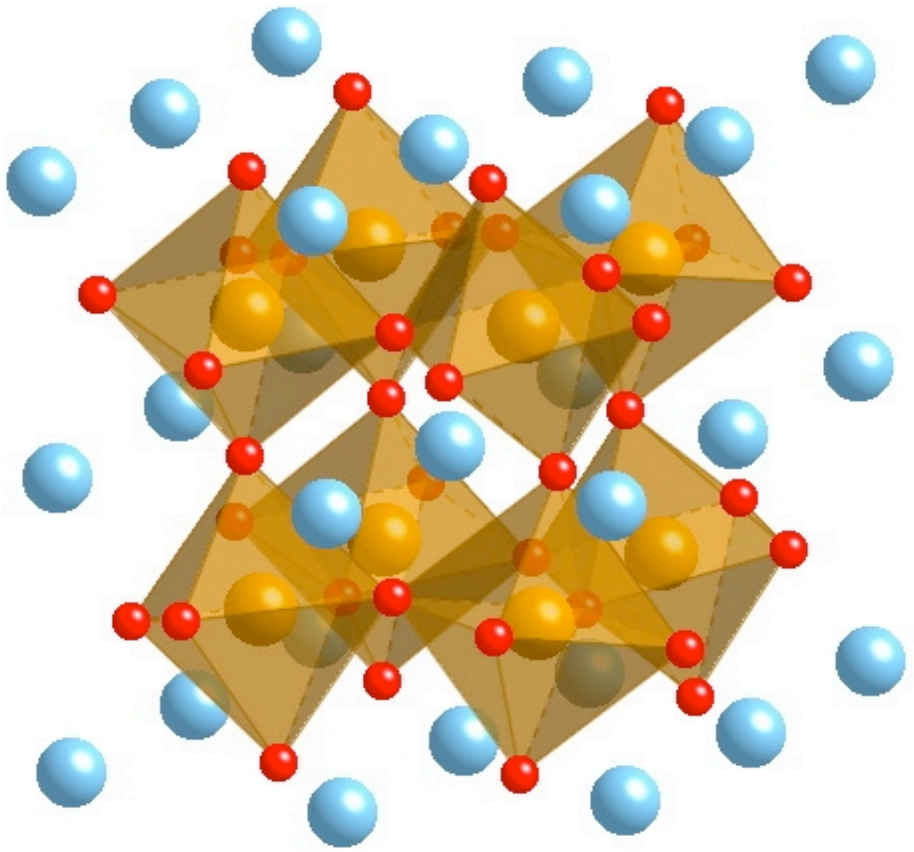
Outline

- 3d perovskite oxides
  - Influence of Temperature and pressure on $CaFeO_3$ crystal
- Embedded cluster approach
- Pressure induced high spin to low spin transition
  - Unitary transformation of the active orbitals
  - Charge transfer with increasing pressure
- Charge Disproportionation
- Analysis of Mössbauer spectroscopy
- Conclusions

3d perovskite oxides



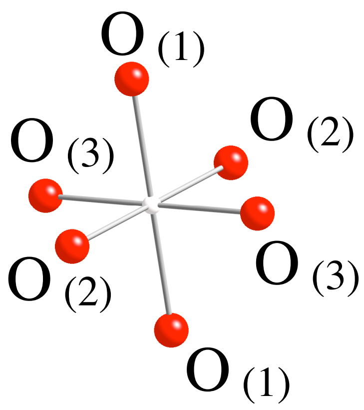
ABO$_3$

A^{n+} Cation site

BO_6^{n-} Octahedron of TM

Ionic model :

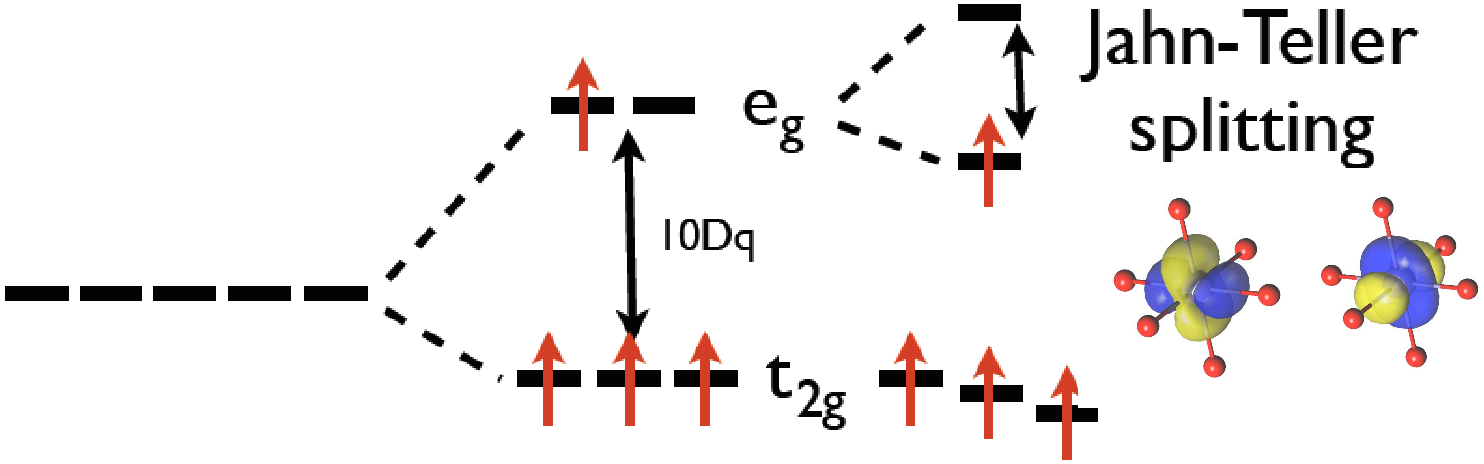
A^{n+}, O^{2-} → Closed shell ions



Jahn-Teller distortion

LaMnO$_3$ Mn^{3+} 3d^4 Pbnm T_{JT} = 750 K

d^4 systems → Jahn-Teller distortion is expected



Jahn-Teller splitting

Spherical symmetry

Octahedral field

Charge disproportionation

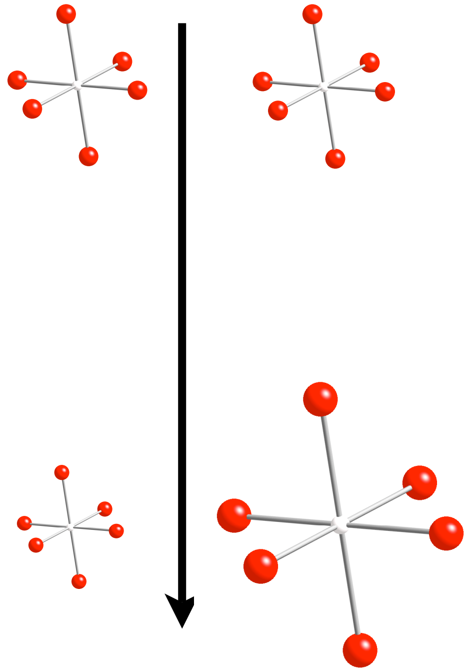
CaFeO$_3$ Fe^{4+} 3d^4 Pbnm to $P2_1/n$ T_{CD} = 298 K

Table I: metal-ligand bond lenghts in angstrom.

	LaMnO$_3$		CaFeO$_3$		
T	**300 K**	798 K	**15K Fe$_I$**	**15 K Fe$_{II}$**	300 K
TM-O(1)	**1.968**	2.010	**1.853**	**1.997**	1.920
TM-O(2)	**1.907**	1.998	**1.870**	**1.971**	1.920
TM-O(3)	**2.178**	2.035	**1.894**	**1.953**	1.918

Influence of temperature on $C_aF_eO_3$ crystal

Mössbauer spectroscopy



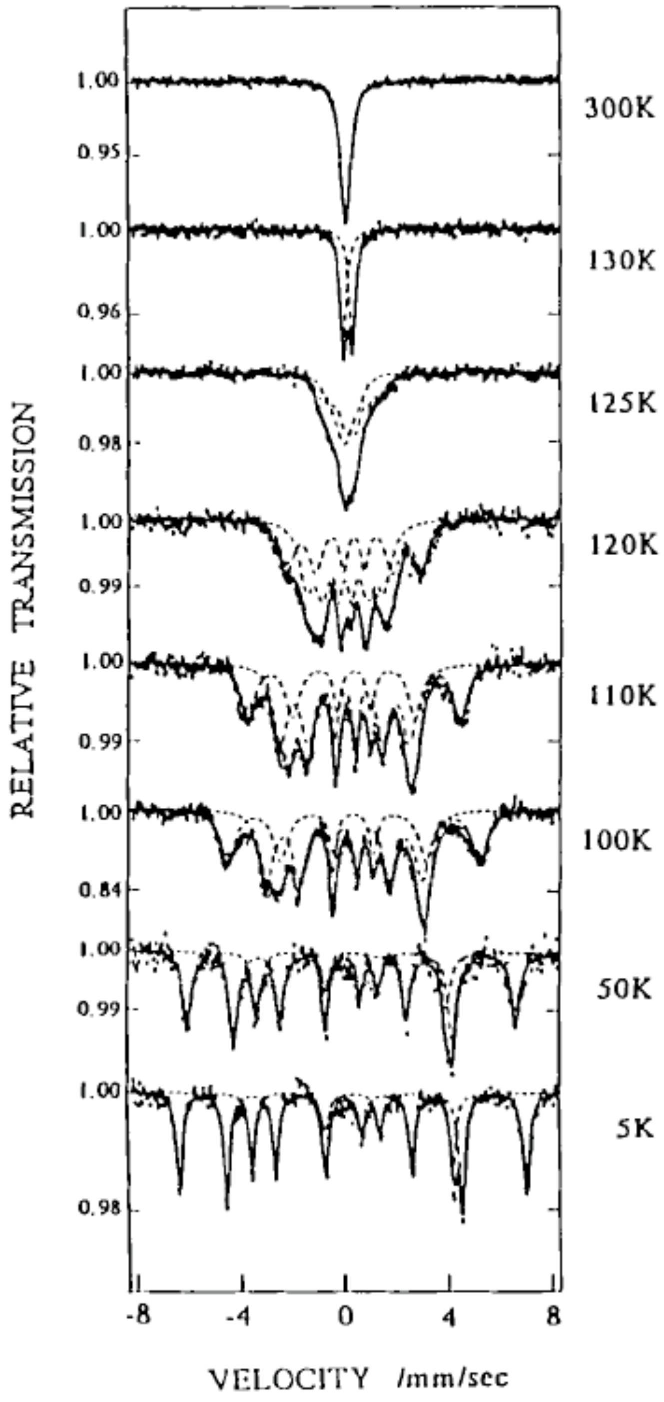
0.048 mm/s

$Fe^{4+}–O–Fe^{4+}$

$Fe^{5+}–O–Fe^{3+}$

-0.026 mm/s

0.310 mm/s



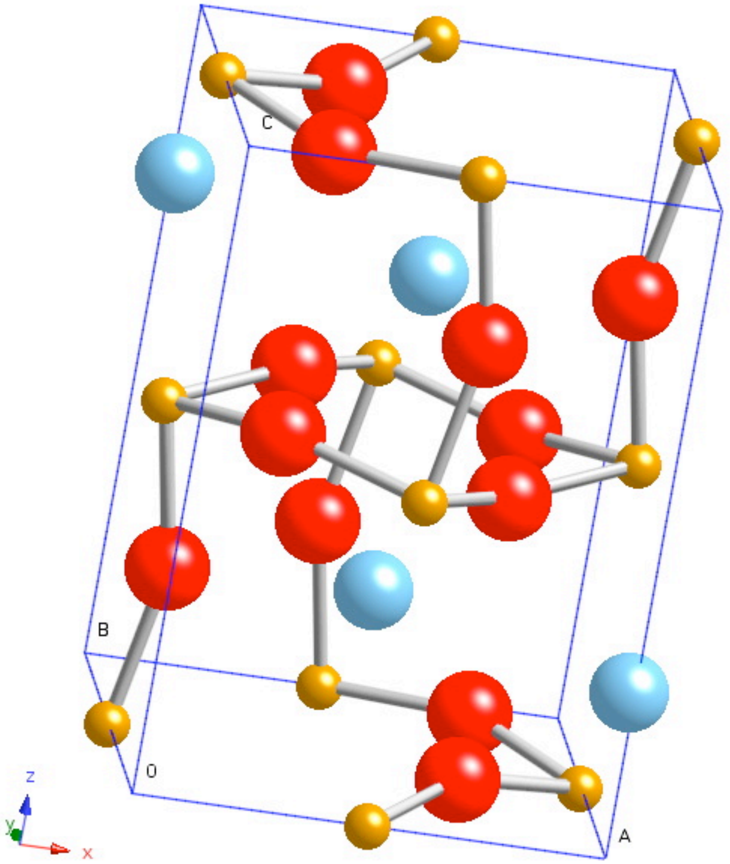
Nasu et al, Hyperfine Interactions (1992)

Influence of pressure on $C_aF_eO_3$ crystal

X-ray diffraction

$CaFeO_3$ lattice parameters and average Fe-O distance in Angstrom with increasing pressure. The parameters are deduced from *Woodward et al, PRB (2000)* for 0.1 GPa and Fig. 2 in *Takano et al, PRL (1991)* for larger pressure.

	0.1 GPa	10 GPa	20 GPa	30 GPa	40 GPa	50 GPa
a	5.31744	5.24673	5.17602	5.09117	5.16195	5.16100
b	5.31744	5.24673	5.17602	5.09117	4.89325	4.83668
c	7.52000	7.42000	7.32000	7.20000	7.20010	7.09000
Fe-O	1.918	1.889	1.865	1.833	1.819	1.803



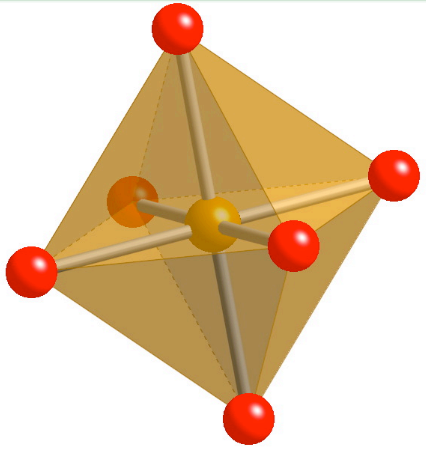
Mössbauer spectroscopy

The ambient pressure spectrum consists of a single narrow line with a chemical shift of 0.048 mm/s.

Chemical shift is reduced abruptly at 30 GPa by 0.25 mm/s

↳ Pressure induced high spin to low spin transition

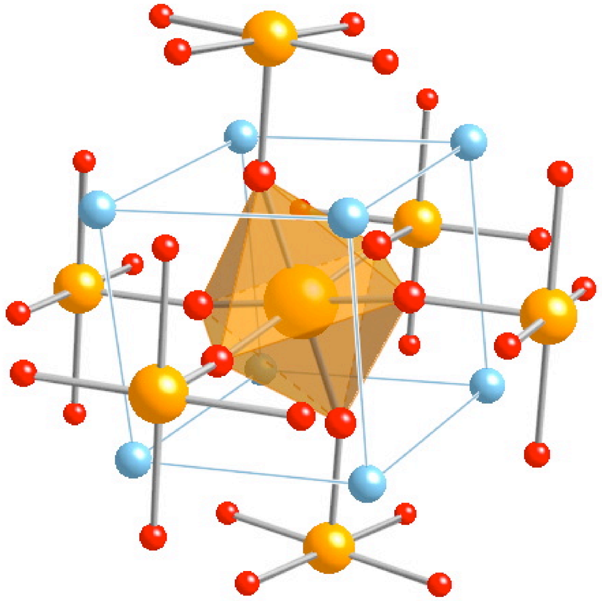
Embedded cluster approach : Material model



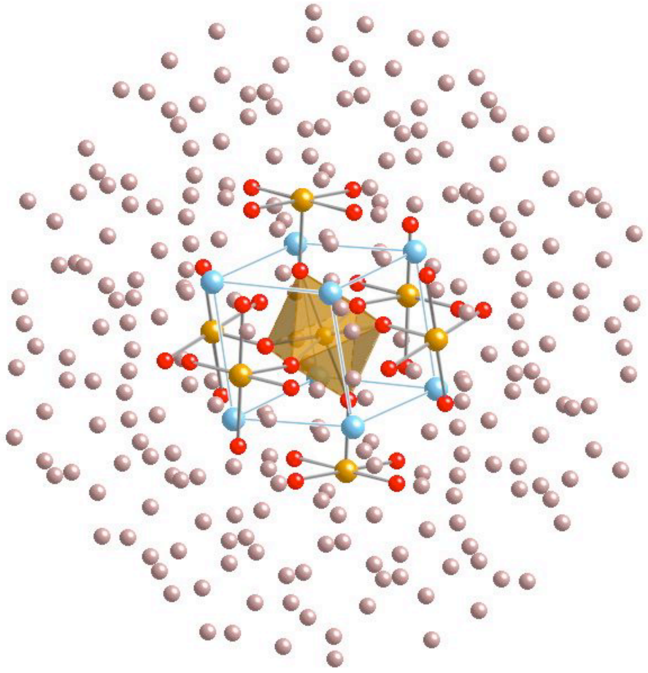
Basic Cluster: MLn

Basis set : O 4s3p1d ANO
Fe 6s5p4d1f ANO

χ_k

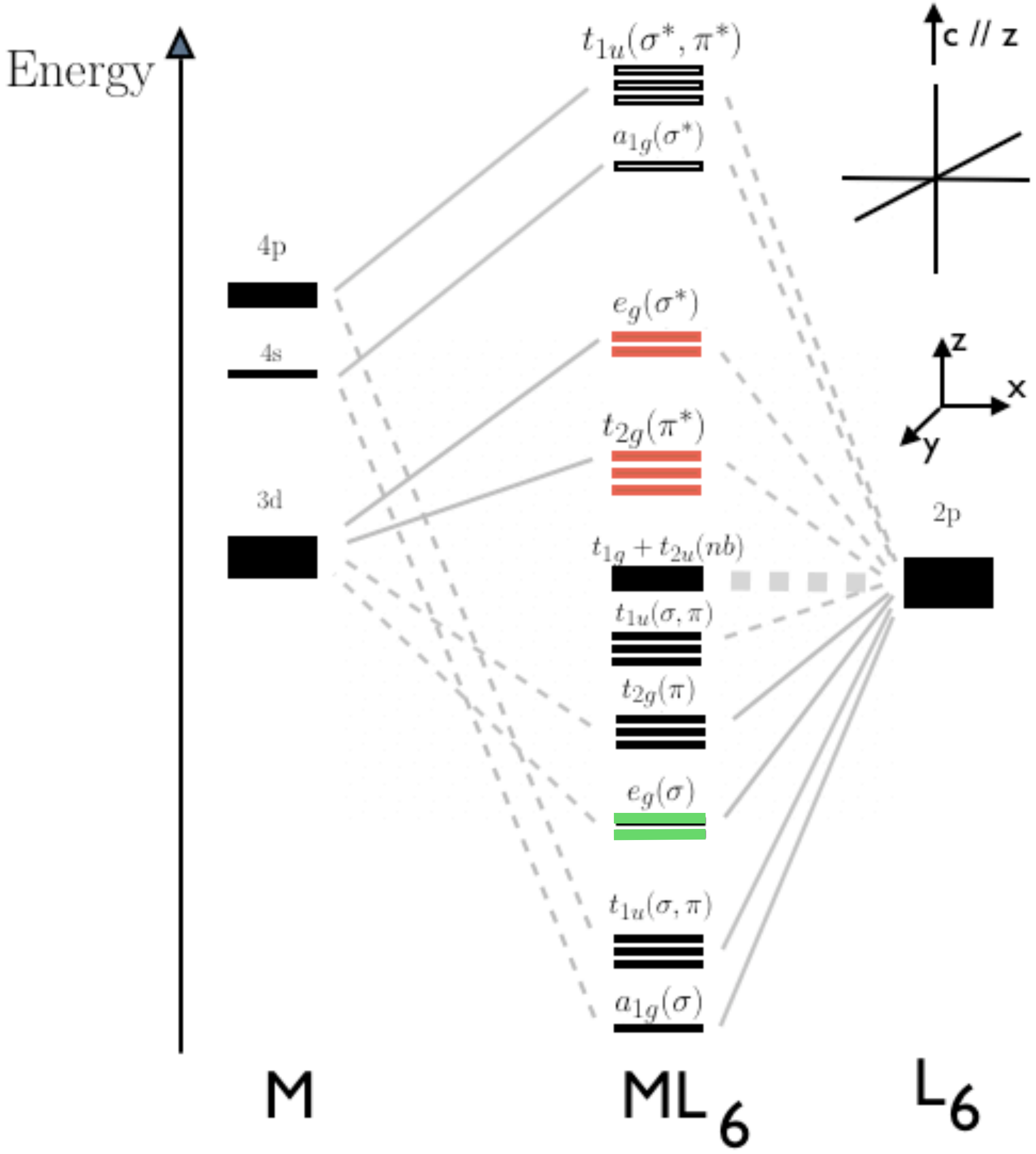


Model Potentials: *ab initio* Embedded Model Potentials AIEMP (based on Theory of Electron Separability).



Point charges: long range electrostatic interactions with a set of optimizied point charges to reproduce the Madelung field in the cluster region arising from the rest of the crystal.

Embedded cluster approach : Cluster wave function



SCF : single determinant description of the electronic function

Molecular orbitals $\varphi_i = \sum_k \lambda_{ki} \cdot \chi_k$

Determinant $\phi_j = \mid \varphi_1 \varphi_2 \ldots \varphi_N \rangle$

HF solution $E = min_{\lambda_{ki}} \dfrac{\langle \phi \mid \hat{H} \mid \phi \rangle}{\langle \phi \mid \phi \rangle}$

CASSCF : Adequate description of the electron distribution

$$\mid \Psi_m \rangle = \sum_l c_{lm} \mid \Phi_l \rangle$$

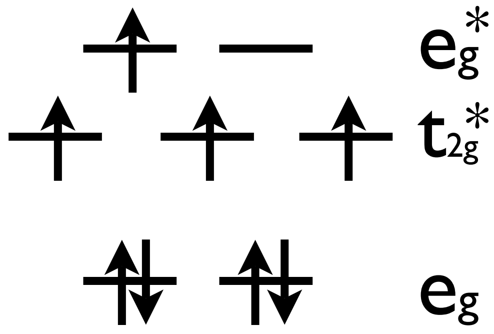
$$E = min_{c_{lm}, \lambda_{ki}} \frac{\langle \Psi \mid \hat{H} \mid \Psi \rangle}{\langle \Psi \mid \Psi \rangle}$$

CASPT2 : Accurate description of the relative energies of the different electronic states (Perturbation method applied on the CASSCF wave function)

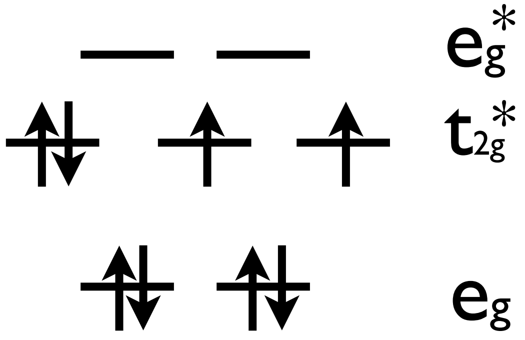
Influence of active space definition

$CaFeO_3$ Fe^{4+} Pbnm T = 298 K; P = 0.1 GPa

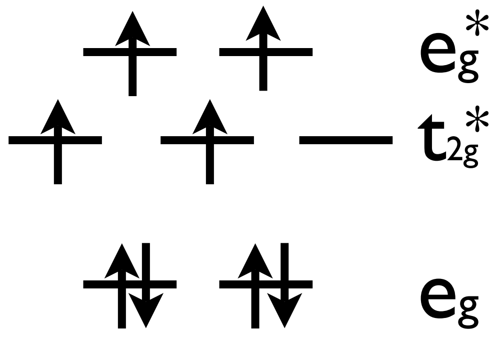
State	Dominant electronic configuration	CAS(8,12)SCF + CASPT2
^5E_g	$e_g^4\ t_{2g}^{*3}\ e_g^{*1}$	0.00 ; 0.04
a^3T_{1g}	$e_g^4\ t_{2g}^{*4}\ e_g^{*0}$	0.46 ; 0.50 ; 0.52
$^1T_{2g}$	$e_g^4\ t_{2g}^{*4}\ e_g^{*0}$	1.98 ; 1.99 ; 2.02
^1E_g	”	2.16 ; 2.19
^3E_g	$e_g^4\ t_{2g}^{*3}\ e_g^{*1}$	2.26 ; 2.30
b^3T_{1g}	”	2.72 ; 2.72 ; 2.74
$^3T_{2g}$	”	2.82 ; 2.82 ; 2.82
$^5T_{2g}$	$e_g^4\ t_{2g}^{*2}\ e_g^{*2}$	3.42 ; 3.43 ; 3.47



^5E_g



$^3T_{1g}$



$^5T_{2g}$

Pressure induced High spin to low spin transition

Takano et al, PRL (1991)

	0.1 GPa	10 GPa	20 GPa	30 GPa	40 GPa	50 GPa
a	5.31744	5.24673	5.17602	5.09117	5.16195	5.16100
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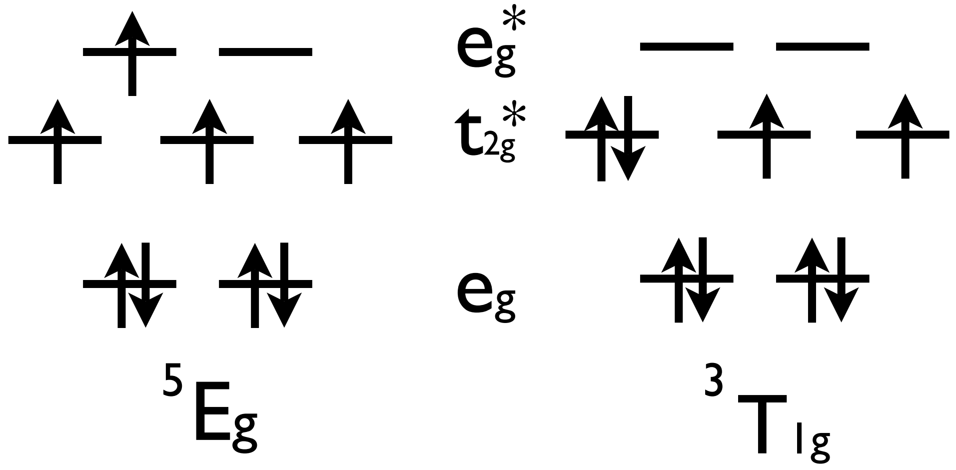
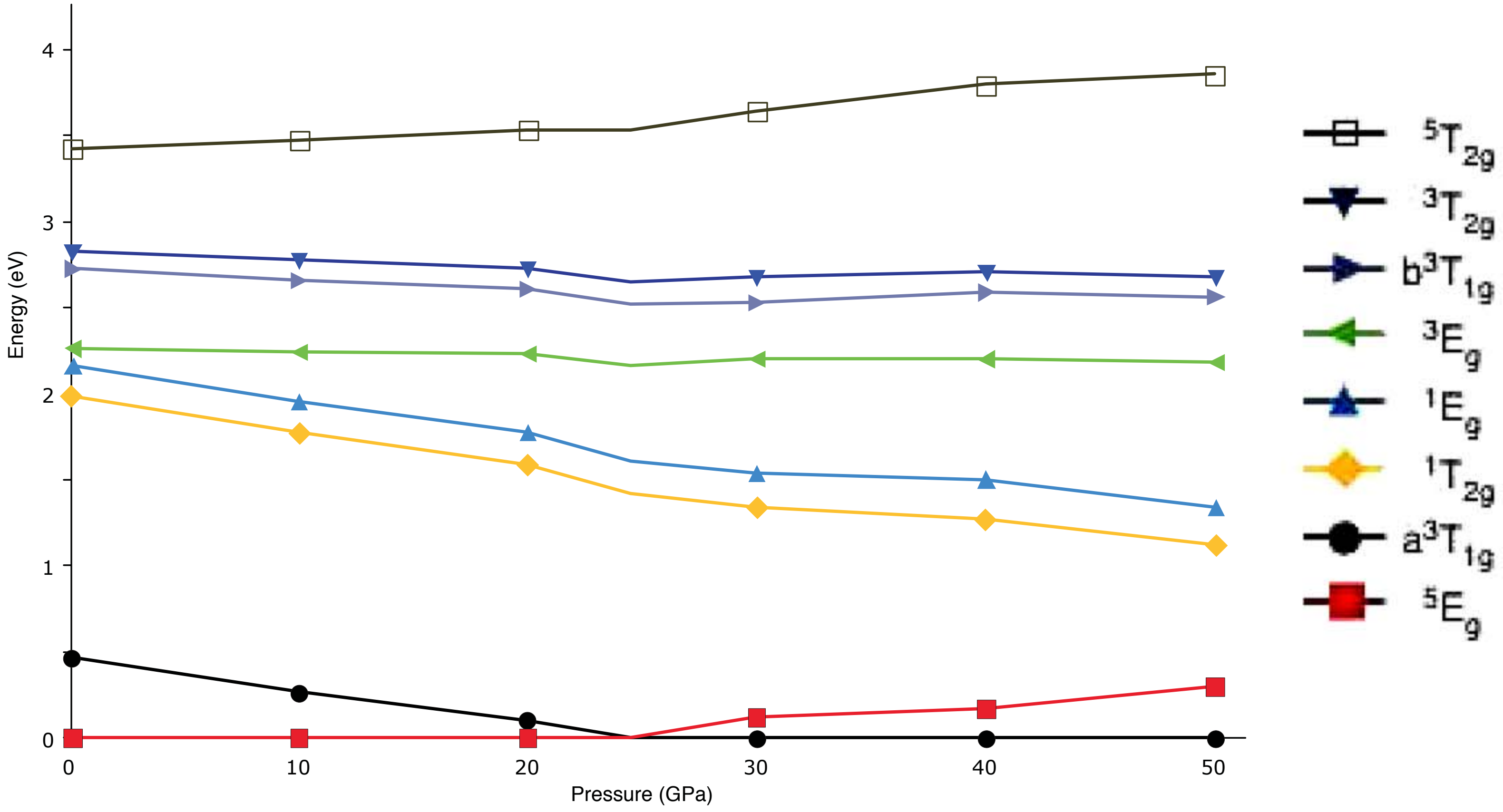
Fe-O	1.918	1.889	1.865	1.833	1.819	1.803



CAS(8,12)SCF + CASPT2



A. Sadoc, C. de Graaf and R. Broer, PRB, 75, 165116 (2007)

CASPT2 energies follow closely the Tanabe-Sugano diagram for a d^4 ion in octahedral field.

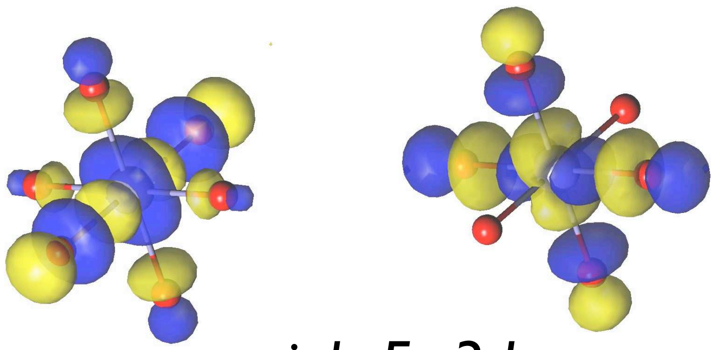
At 25 GPa the $^3T_{1g}$ state becomes the ground state of the system.

Agreement with experimental interpretation of the high spin to low spin transition for increasing pressure.

Unitary transformation

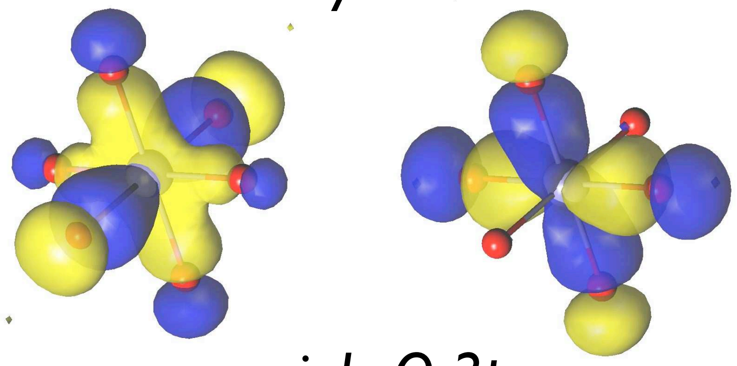
CaFeO_3 Fe^{4+} d^4 Pbnm to $P2_1/n$ T_{CD} = 298 K

e_g^*



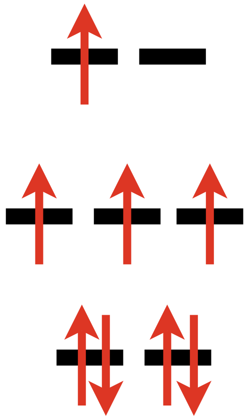
mainly Fe-3d

e_g



mainly O-2p

Natural orbitals



e_g^* 85.8 % $e_g^4\, t_{2g}^{*3}\, e_g^{*1}$

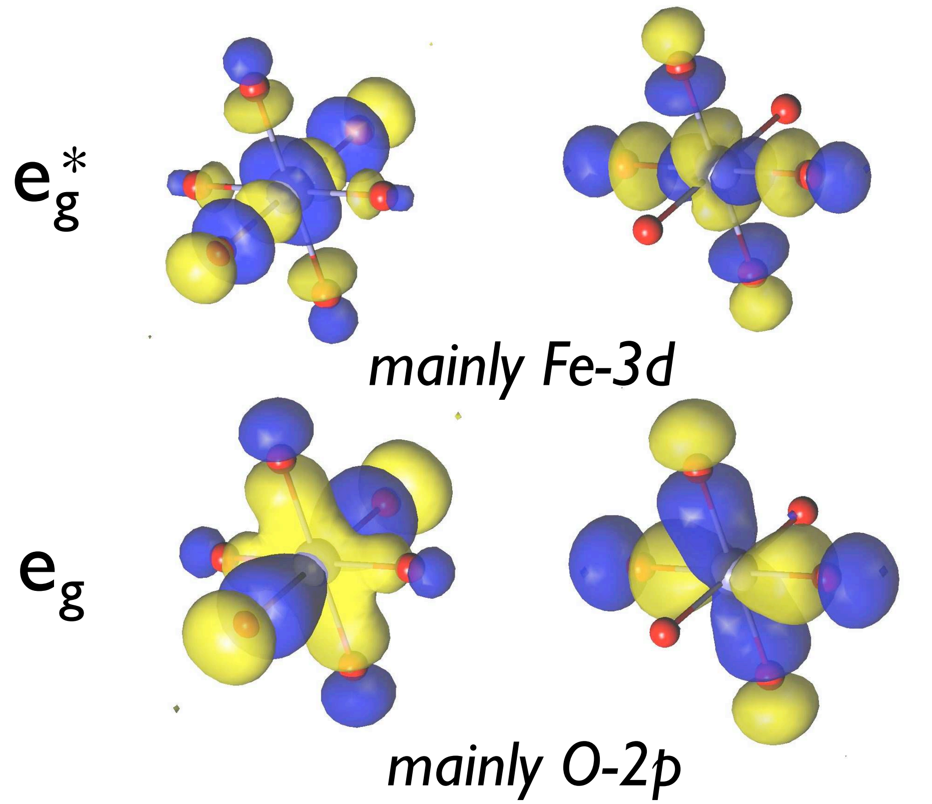
t_{2g}^* 7.2 % $e_g^3\, t_{2g}^{*3}\, e_g^{*2}$

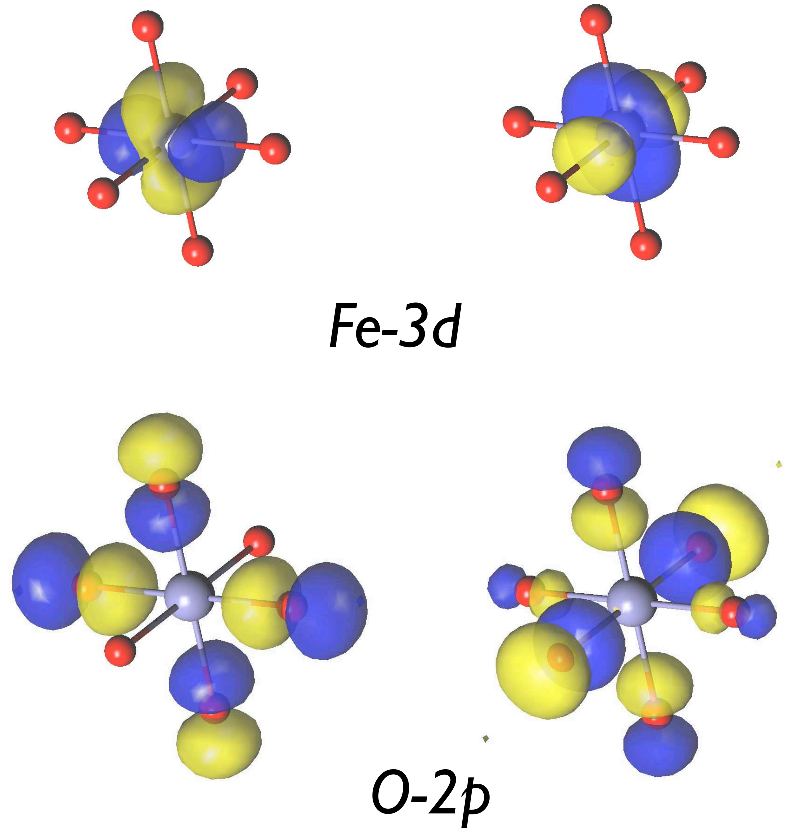
e_g 4.4 % $e_g^2\, t_{2g}^{*3}\, e_g^{*3}$

Formal charge = +4 ⟶ ^5E_g Ground state

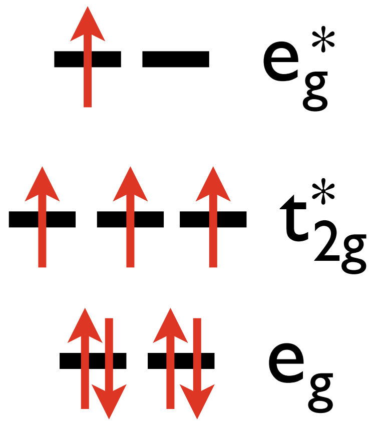
Unitary transformation

$CaFeO_3$ Fe^{4+} d^4 Pbnm to $P2_1/n$ T_{CD} = 298 K CAS(8,12) or cas-pdd ^5E_g first root





Natural orbitals



85.8 % $e_g^4\ t_{2g}^{*3}\ e_g^{*1}$

7.2 % $e_g^3\ t_{2g}^{*3}\ e_g^{*2}$

4.4 % $e_g^2\ t_{2g}^{*3}\ e_g^{*3}$

Formal charge = +4 ⟶ ^5E_g Ground state

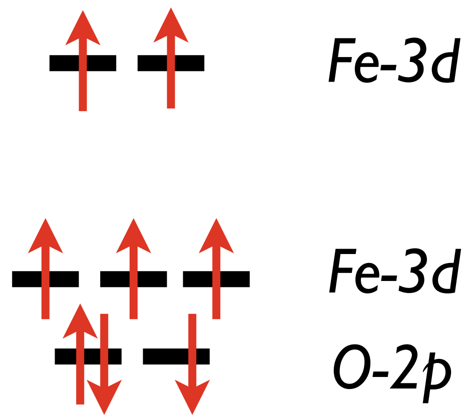
A. Sadoc, C. de Graaf and R. Broer, JCP, 126, 134709 (2007)

Atomic-like orbitals

18.9 % NCT d^4

66.2 % CT d^5L^{-1}

13.9 % DCT d^6L^{-2}



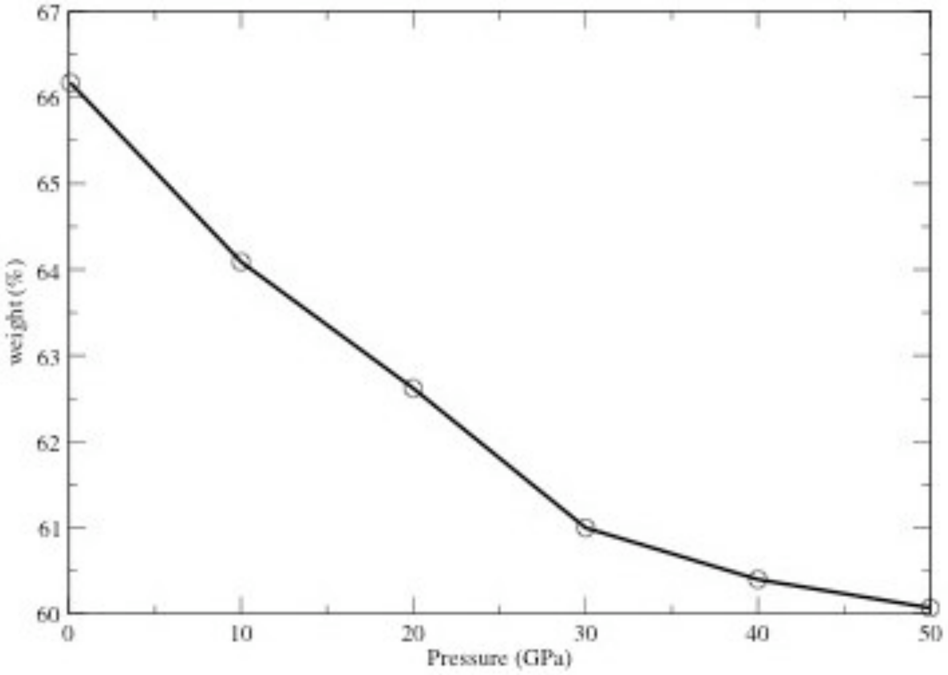
Effective number of Fe-3d electrons = 4.9

Effective charge = +3

GS corresponds to more than 60 % of CT meaning that Fe ions are Fe^{3+} with mainly d^5 L^{-1} configuration

Evolution of charge transfer with increasing pressure

	Pressure	NCT	CT	DCT	TCT	Fe-3d^x
^5E_g	0.1	18.9	66.2	14.0	0.4	4.93
	10	21.1	64.1	13.7	0.4	4.90
	20	22.3	62.6	14.0	0.4	4.89
	30	23.6	61.0	14.3	0.5	4.89
	40	20.5	60.4	18.6	0.9	4.96
	50	22.9	60.1	15.8	0.7	4.92
a^3T_{1g}	0.1	12.7	55.4	28.4	2.0	5.12
	10	13.8	54.9	27.6	2.1	5.10
	20	14.5	54.5	27.2	2.2	5.09
	30	15.3	53.7	27.0	2.4	5.09
	40	15.3	53.3	27.3	2.5	5.09
	50	13.1	51.1	30.5	3.7	5.17



Clear decrease of CT configurations in the ^5E_g when the pressure is increased.

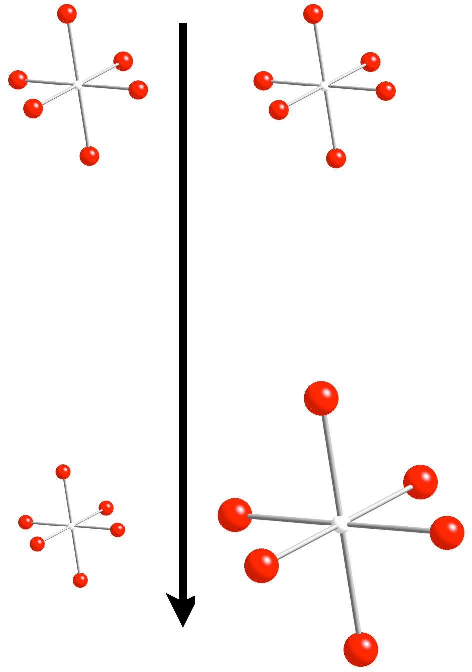
In the whole pressure range, the number of Fe-3d electrons is around 5.

For the triplet state, the NCT is less important and the DCT becomes twice as important compared to the Eg state

Charge Disproportionation

0.048 mm/s

$\mathrm{Fe^{4+}{-}O{-}Fe^{4+}}$

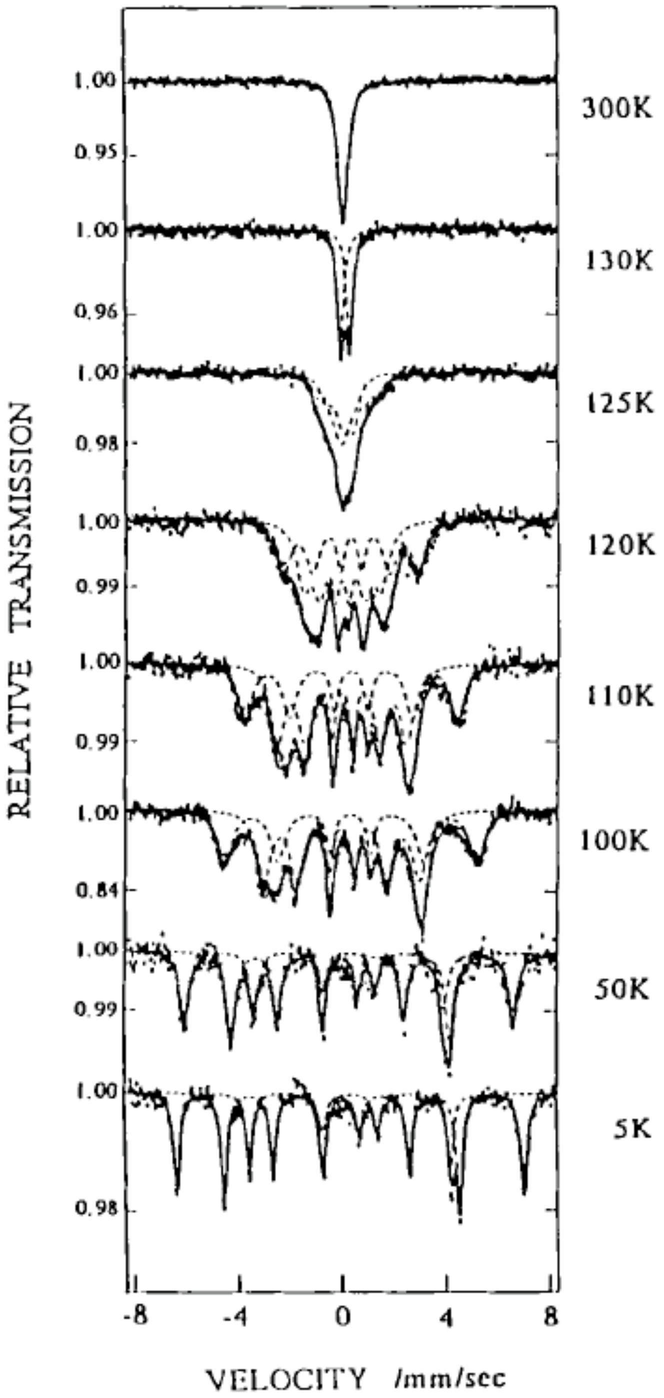


$\mathrm{Fe^{5+}{-}O{-}Fe^{3+}}$

-0.026 mm/s

0.310 mm/s

Nasu et al, Hyperfine Interactions (1992)

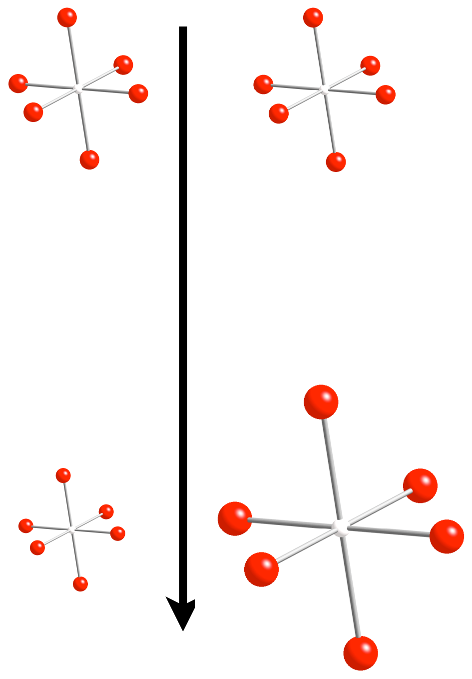


$$d^4 \longrightarrow d^3 + d^5L^{-2}$$

Charge Disproportionation

0.048 mm/s

$Fe^{4+}–O–Fe^{4+}$



$Fe^{5+}–O–Fe^{3+}$

-0.026 mm/s

0.310 mm/s

Nasu et al, Hyperfine Interactions (1992)

Effective number of Fe-3d electrons = 4.9

Actual charge = +3

GS corresponds to more than 60 % of CT meaning that Fe ions are Fe^{3+} with mainly d^5 L^{-1} configuration

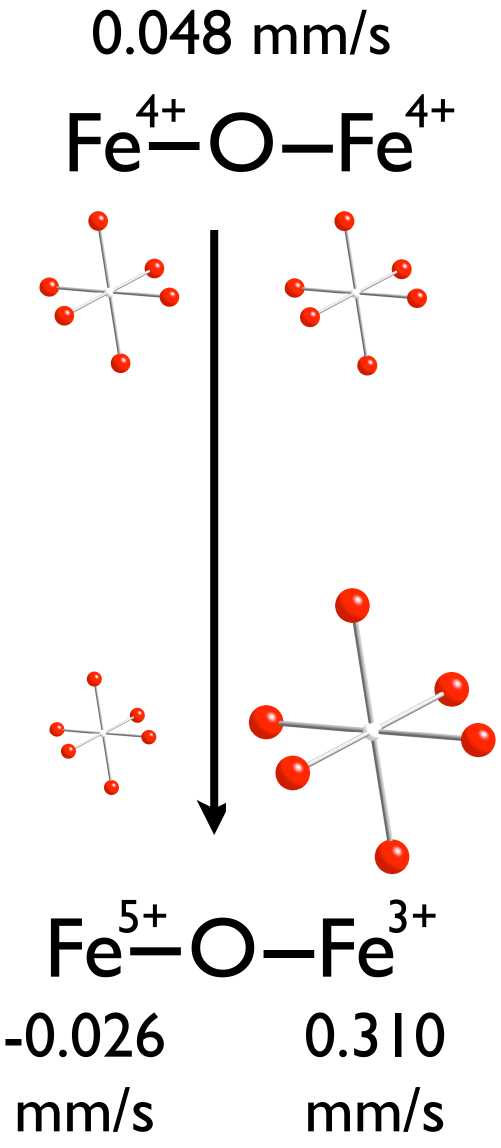
Table IV: Wave function expansion simulating CaFeO3 crystal using embedded clsuter approach

	NCT d^4	CT d^5L^{-1}	DCT d^6L^{-2}	Fe 3d-count
At 298 K, above TCD	18,9	66,2	13,9	4,93

$\xcancel{d^4 \longrightarrow d^3 + d^5L^{-2}}$

d^5L^{-1}

Charge transfer with increasing temperature



0.048 mm/s

$Fe^{4+}-O-Fe^{4+}$

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-0.026 mm/s

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	NCT d^4	CT d^5L^{-1}	DCT d^6L^{-2}	Fe 3d-count
At 298 K, above TCD	18,9	66,2	13,9	4,93
At 15 K small octahedron	13.2	60.9	23.7	5.11
At 15 K large octahedron	9.4	65.3	23.3	5.14

We express the wave function with localized orbitals and calculate the number of electrons in the 3d shell which remains almost identical at 15K than as 300 K. This suggests that the transition metal ions keep the same effective charge in all temperature range.

$$\xcancel{d^4 \longrightarrow d^3 + d^5L^{-2}}$$

$$d^5L^{-1} \longrightarrow d^5L^{-1} + d^5L^{-1}$$

Analysis of Mössbauer spectroscopy

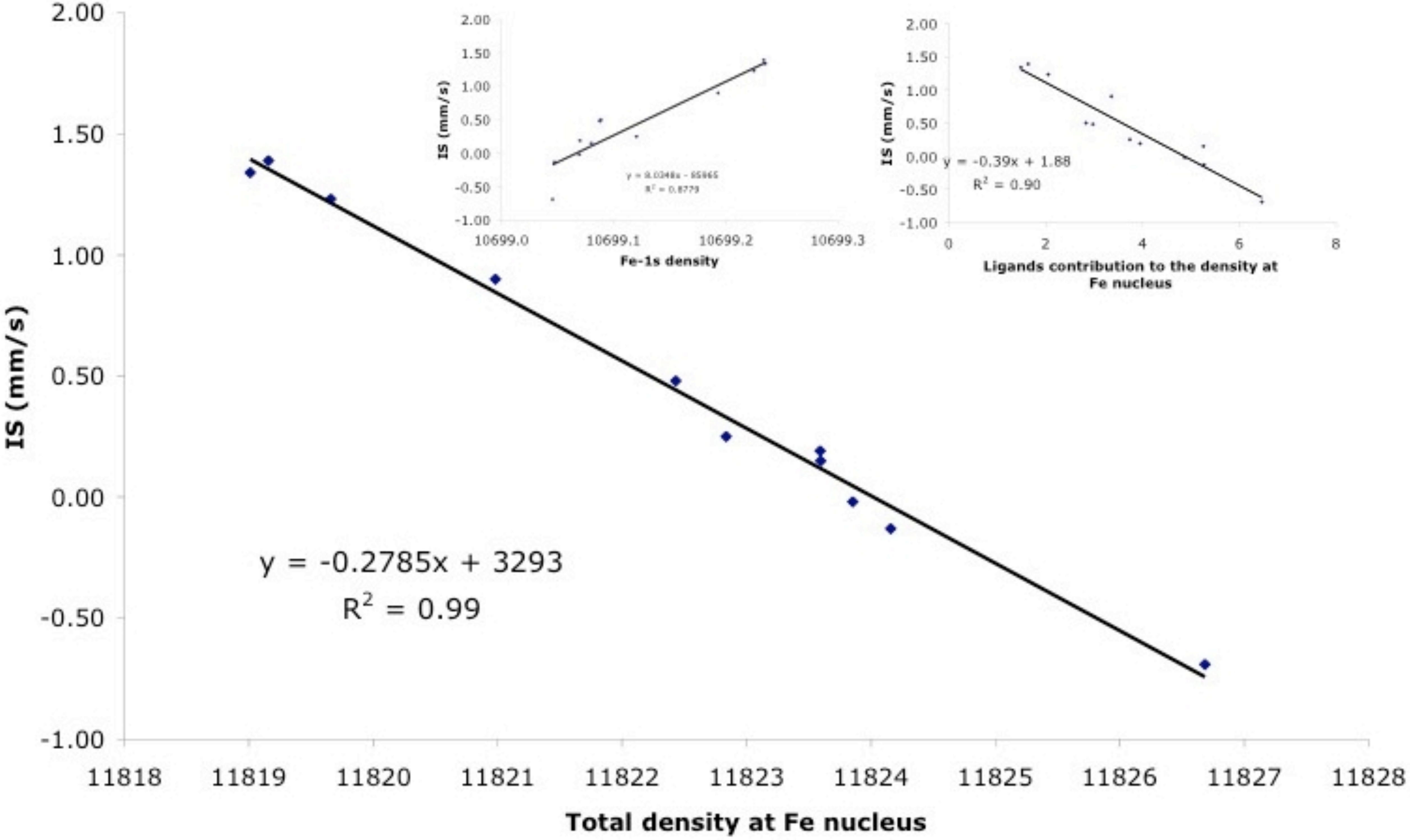
cluster	ρ (Fe)	IS (mm/s)
$Fe(H_2O)_6^{2+}$	11819.158	1.39
FeF_6^{4-}	11819.011	1.34
$FeCl_4^{2-}$	11820.983	0.9
$Fe(H_2O)_6^{3+}$	11822.936	0.5
FeF_6^{3-}	11822.432	0.48
$FeCl_4^{-}$	11823.592	0.19
$Fe(CN)_6^{4-}$	11823.853	-0.02
$Fe(CN)_6^{3-}$	11824.160	-0.13
FeO_4^{2-}	11826.785	-0.69

W. C. Nieuwpoort, D. Post, P.Th. van Duijnen PRB 17, 91 (1978)

F. Neese et al, Inorga Chimica Acta 337, 181 (2002)

T. Liu, T. Lovell, W.-G. Han, and L. Noodleman, Inorg. Chem. 42, 5244 (2002).

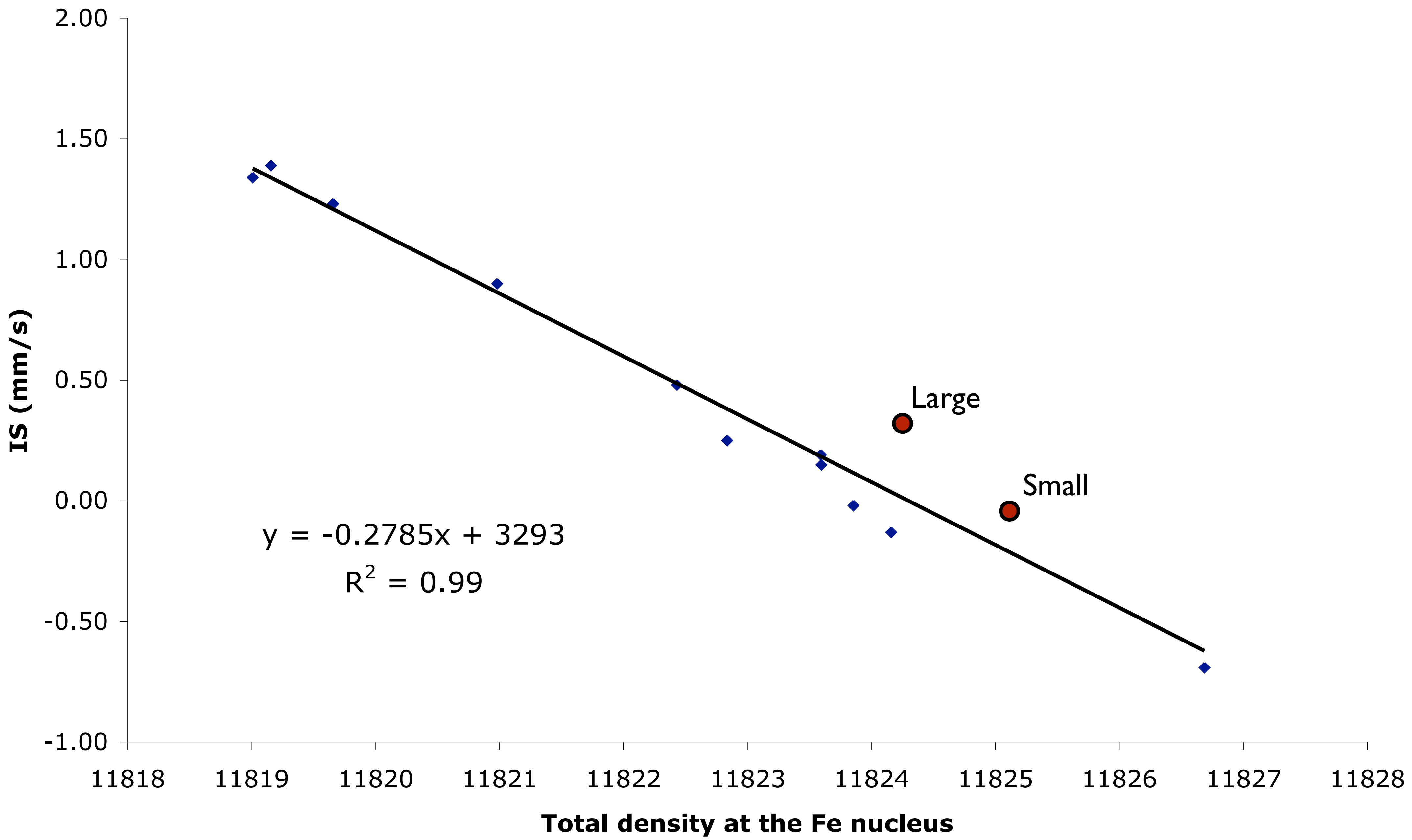
Analysis of Mössbauer spectroscopy



Analysis of Mössbauer spectroscopy

cluster	Formal	Fe 3d-count	Eff charge	IS (mm/s)
$Fe(H_2O)_6^{2+}$	2+	6.05	1.95	1.39
FeF_6^{4-}	2+	6.05	1.95	1.34
$FeCl_4^{2-}$	2+	6.18	1.82	0.9
$Fe(H_2O)_6^{3+}$	3+	5.22	3.78	0.5
FeF_6^{3-}	3+	5.19	3.81	0.48
$FeCl_4^{-}$	3+	5.56	3.44	0.19
$Fe(CN)_6^{4-}$	2+	7.32	1.68	-0.02
$Fe(CN)_6^{3-}$	3+	5.63	3.37	-0.13
FeO_4^{2-}	6+	5.30	3.70	-0.69

Charge disproportionation



Conclusions

Crossing high spin to low spin transition calculated at the CASPT2 level for 25 GPa. In agreement with Mössbauer experiment.

GS corresponds to more than 60 % of CT up to 30 GPa meaning that Fe ions are Fe^{3+} with mainly d^5L^{-1} configuration in $CaFeO_3$ crystal at room temperature.

Clear decrease of CT configurations in the ^5E_g when the pressure is increased.

No change of oxidation state for the Fe ions with increasing temperature in $CaFeO_3$ crystal as suggested by the term charge disproportionation.

Acknowledgments

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Thank you for your attention