PAC study of dynamic hyperfine interactions at ^{111}In-doped Sc_2O_3 semiconductor and comparison with *ab initio* calculations

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Motivations

➢ The inclusion of impurities in semiconductors have broad significance for the basic and applied research.

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➤ The inclusion of impurities in semiconductors have broad significance for the basic and applied research.

➤ The experimental characterizations at impurity sites in oxides have a fundamental importance for the evaluation of the *ab initio electronic structure calculation* predictions of structural and electronic properties in doped systems.

➤ To correctly understand the underlying physics of the phenomenological model used in perturbation factors it is necessary a theoretical study based in first-principles calculations.

Outline

➢ **Studied system**

➢ **PAC technique**

➢ **Experimental results**

➢ **FP-APW+lo calculations**

➢ **Final remarks**

Outline

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➢ Experimental results
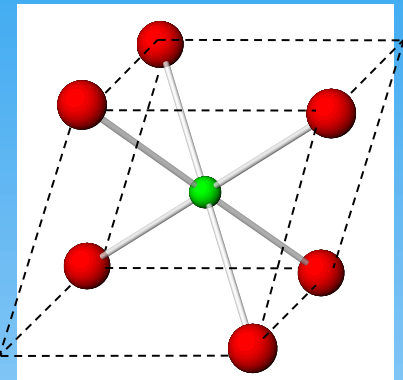
➢ FP-APW+lo calculations

➢ Final remarks

Studied system: Sc$_2$O$_3$

Site _D_

Site _C_

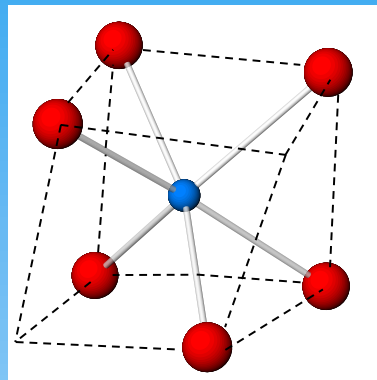• The Sc$_2$O$_3$ oxide crystallizes in the bixbiyte structure and presents two cation sites: C and D.

• The relative abundance is $f_C/f_D=3:1$.

• The ONN coordination is 6 for both sites.

• The D site is axially symmetric and the C site presents high asymmetry.

Studied system: Sc_2O_3

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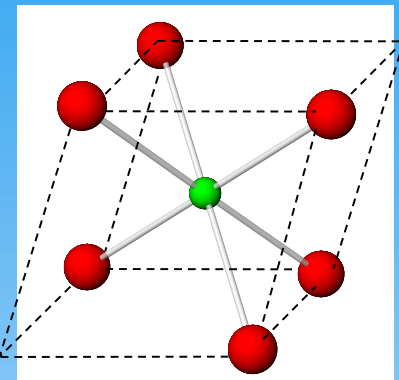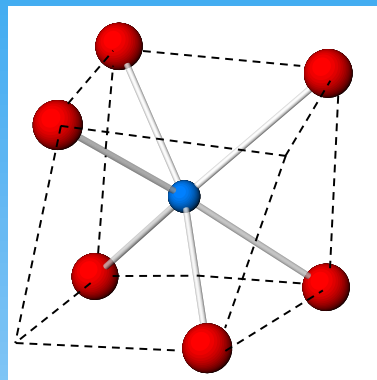• The D site is axially symmetric and the C site presents high asymmetry.

Site D

Site C

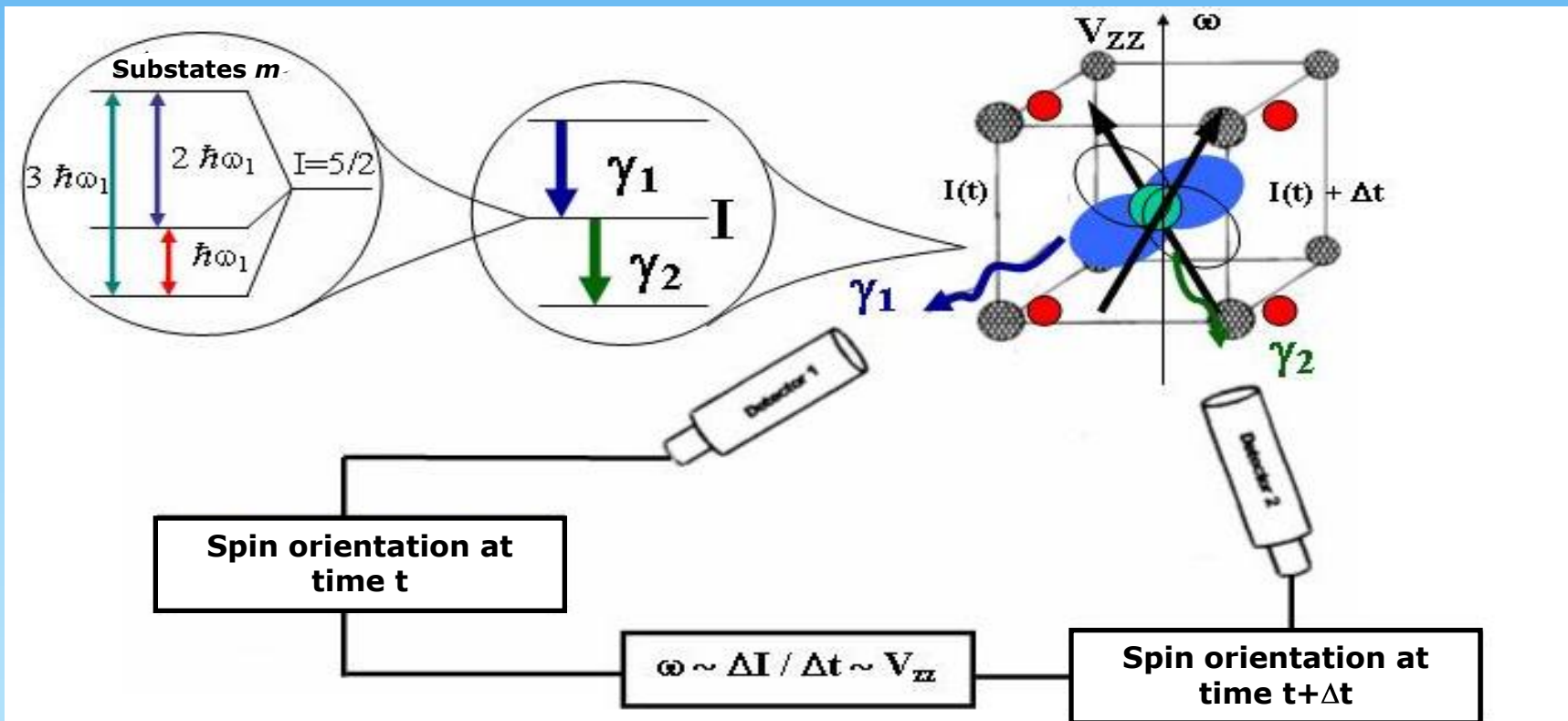| Method	a (Å)	$-u$	x	y	z
Experimental [1]	9.845	0.03546	0.39137	0.15477	0.38137
FP-APW+lo (LDA)	9.708	0.0364	0.3915	0.1545	0.3810
FP-APW+lo (WC-GGA)	9.798	0.0361	0.3913	0.1543	0.3812

[1] M. Marezio, Acta Cryst. **20**, 723 (1966).

Outline

PAC technique

$$G_{22}^s(t) = S_{20}(\eta) + \sum_{n=1}^{3} S_{2n}(\eta)\cos(\omega_n(\eta,\omega_Q)t)$$

$$R(t) = 2\frac{C(180°,t) - C(90°,t)}{C(180°,t) + 2C(90°,t)} \quad, \quad \omega_Q = \frac{eQV_{33}}{40\hbar} \quad, \quad \eta = \frac{V_{11} - V_{22}}{V_{33}}$$

^{111}Cd probe and sample preparation

➤ Some drops of ^{111}InCl$_3$ were deposited onto a Sc$_2$O$_3$ (99.999% purity) powder pellet. The ^{111}In thermal diffusion was performed in N$_2$ atmosphere (3x10^8 Pa) in steps from 423 K to 1073 K. The temperature dependence of the EFG was measured in the temperature range 10 K – 900 K.
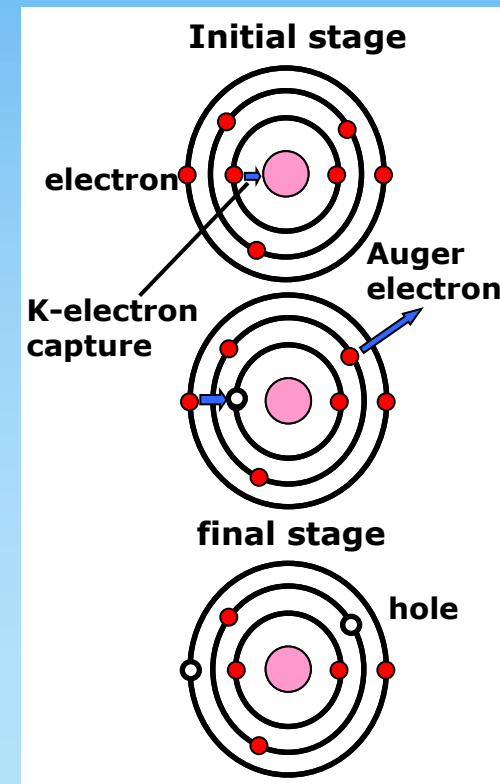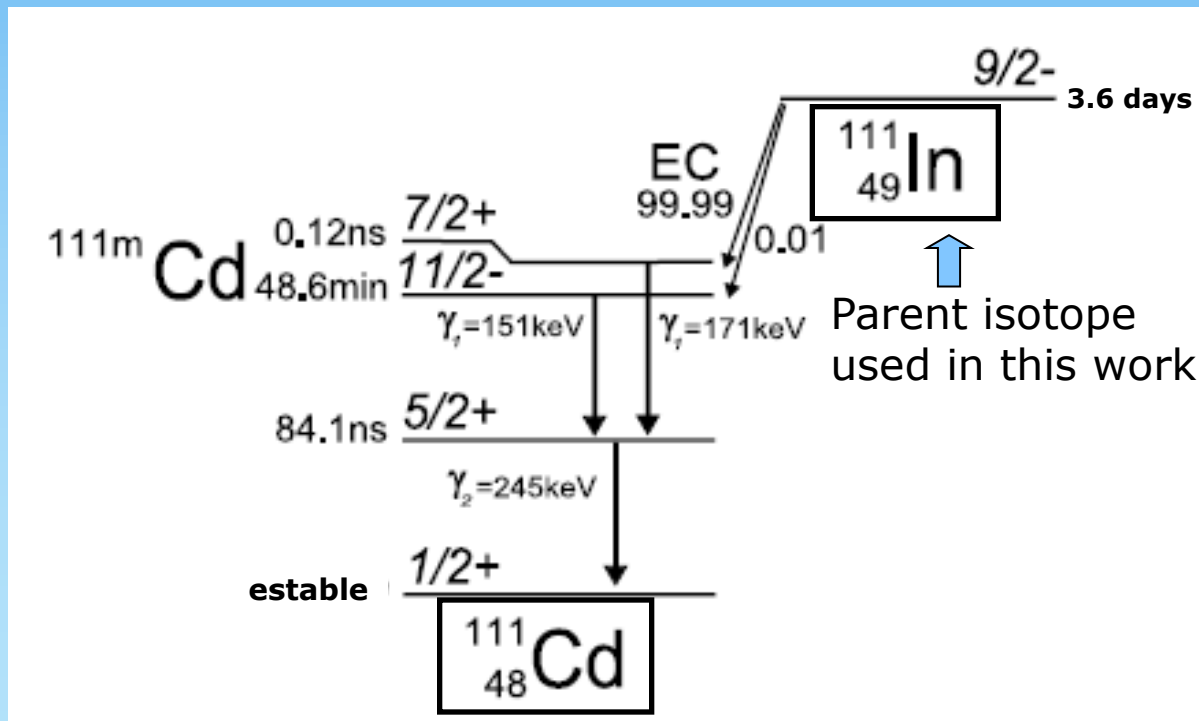
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Parent isotope used in this work

Dynamic Hyperfine Interactions:
Bäverstam and Othaz model

$$G_{22}(t) = G_{22}^{s}(t) \cdot G_{22}^{d}(t)$$

λ_r: Abragam and Pound constant

λ_g: recovery constant ($\lambda_g^{-1} = \tau_g$)

$$\lambda_g = \gamma(1-\alpha)$$

$$\lambda_r = \alpha\gamma$$

$$G_{22}^{d}(t) = \frac{\lambda_g}{\lambda_g + \lambda_r} + \frac{\lambda_r}{\lambda_g + \lambda_r} e^{-(\lambda_g + \lambda_r)t}$$

$$\Longleftrightarrow$$

$$\alpha = \frac{\lambda_r}{\lambda_g + \lambda_r}$$

$$\gamma = \lambda_g + \lambda_r$$

$$G_{22}^{d}(t) = (1-\alpha) + \alpha e^{-\gamma t}$$

Dynamic Hyperfine Interactions:
Bäverstam and Othaz model

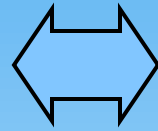$$G_{22}(t) = G_{22}^{s}(t) \cdot G_{22}^{d}(t)$$

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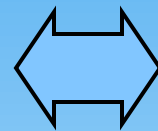
$$\alpha = \frac{\lambda_r}{\lambda_g + \lambda_r}$$

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State with electronic holes
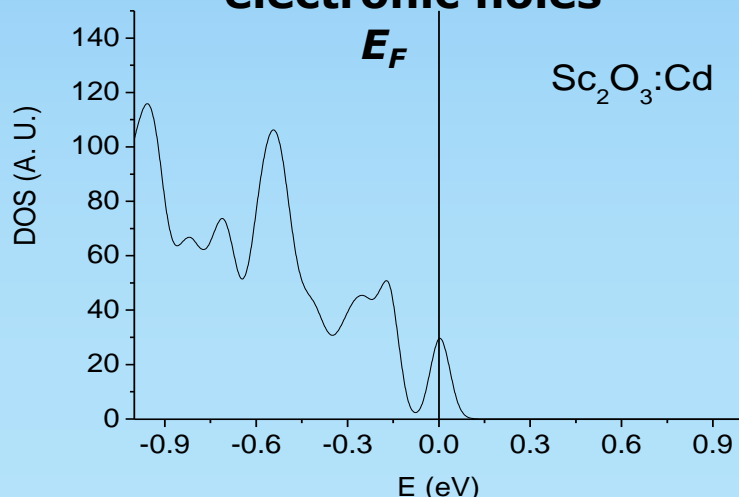
State without electronic holes
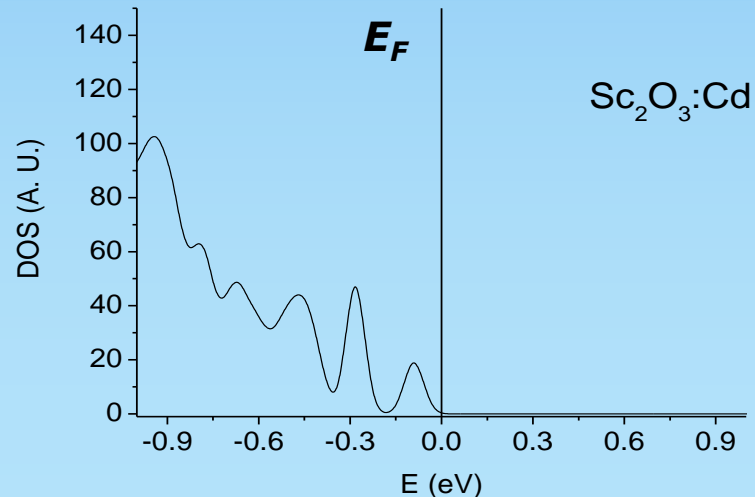
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PAC spectra of ^{111}In-doped Sc_2O_3
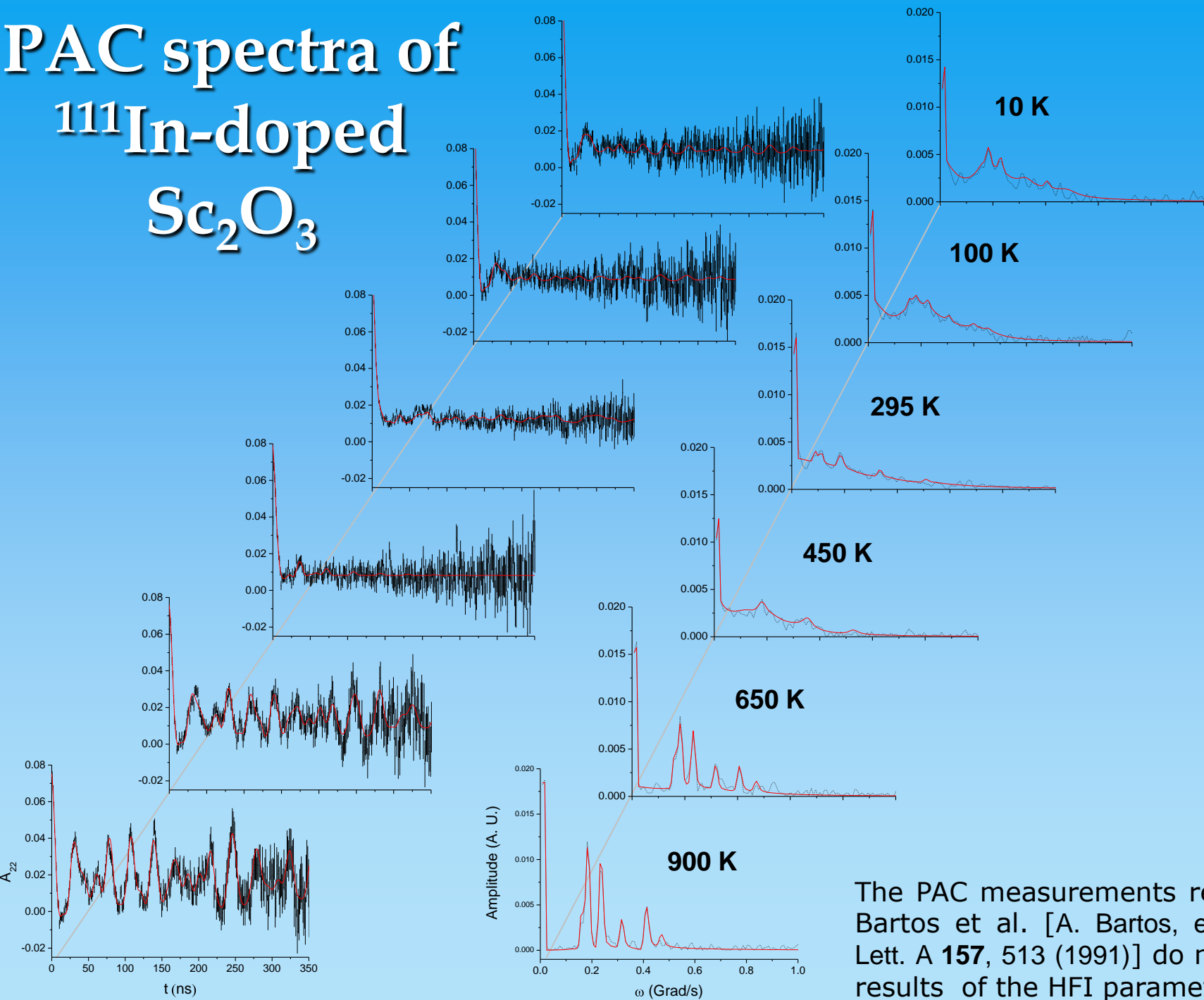
The PAC measurements reported by Bartos et al. [A. Bartos, et al., Phys. Lett. A **157**, 513 (1991)] do not present results of the HFI parameters vs. T.

Hyperfine Parameters vs. T
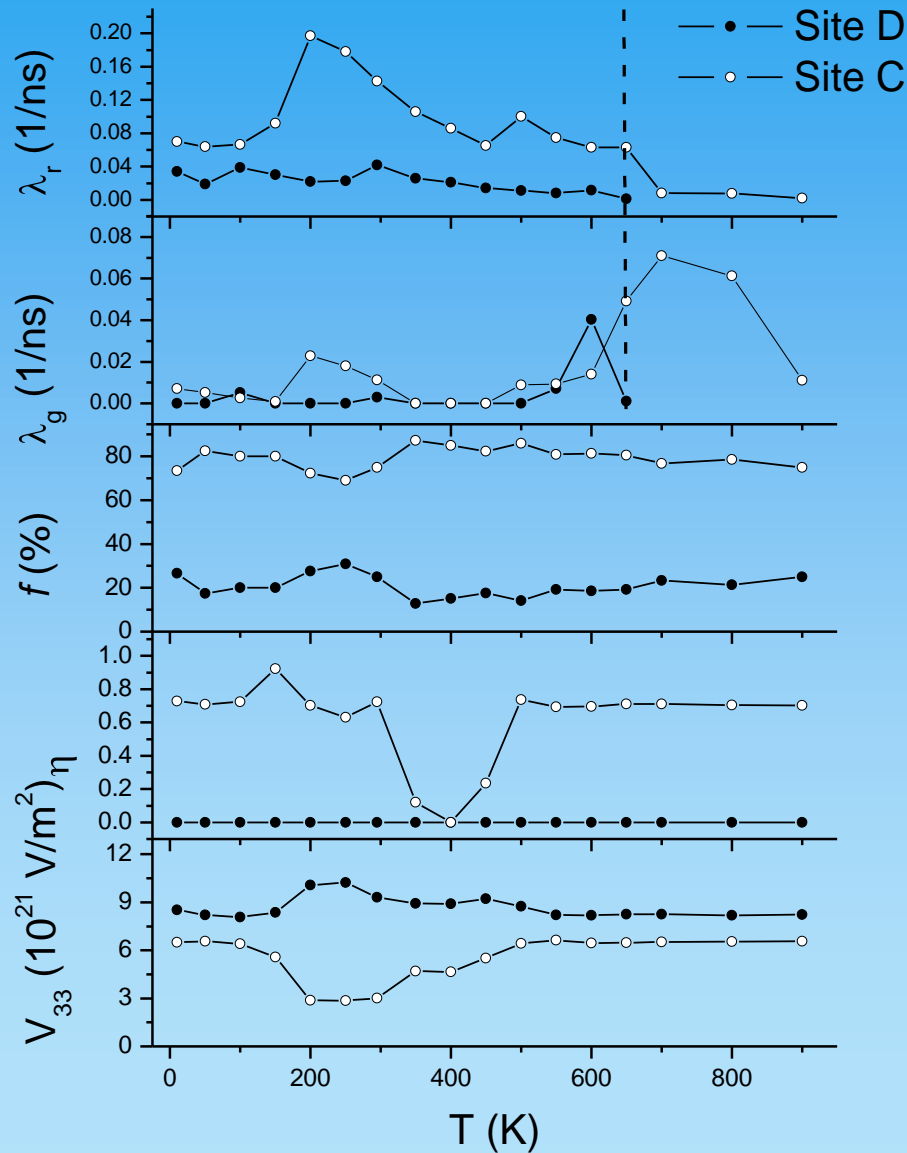
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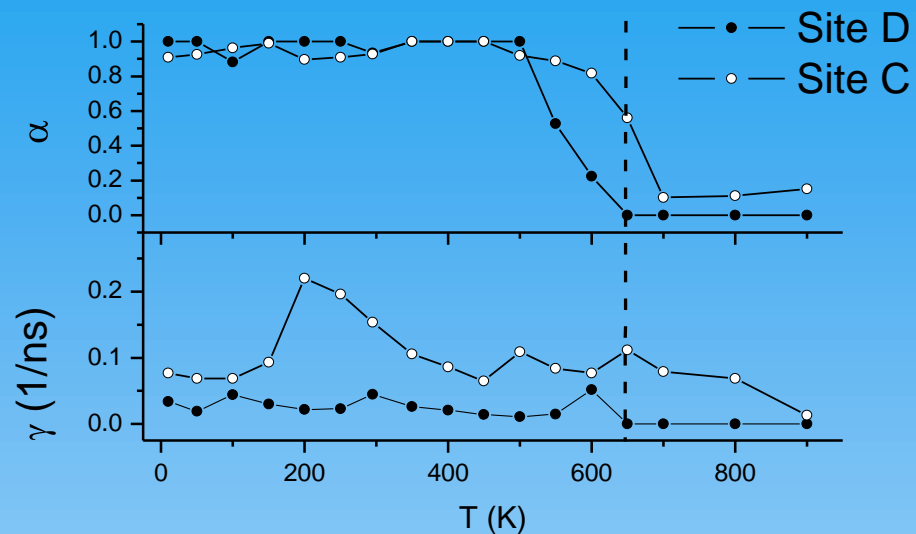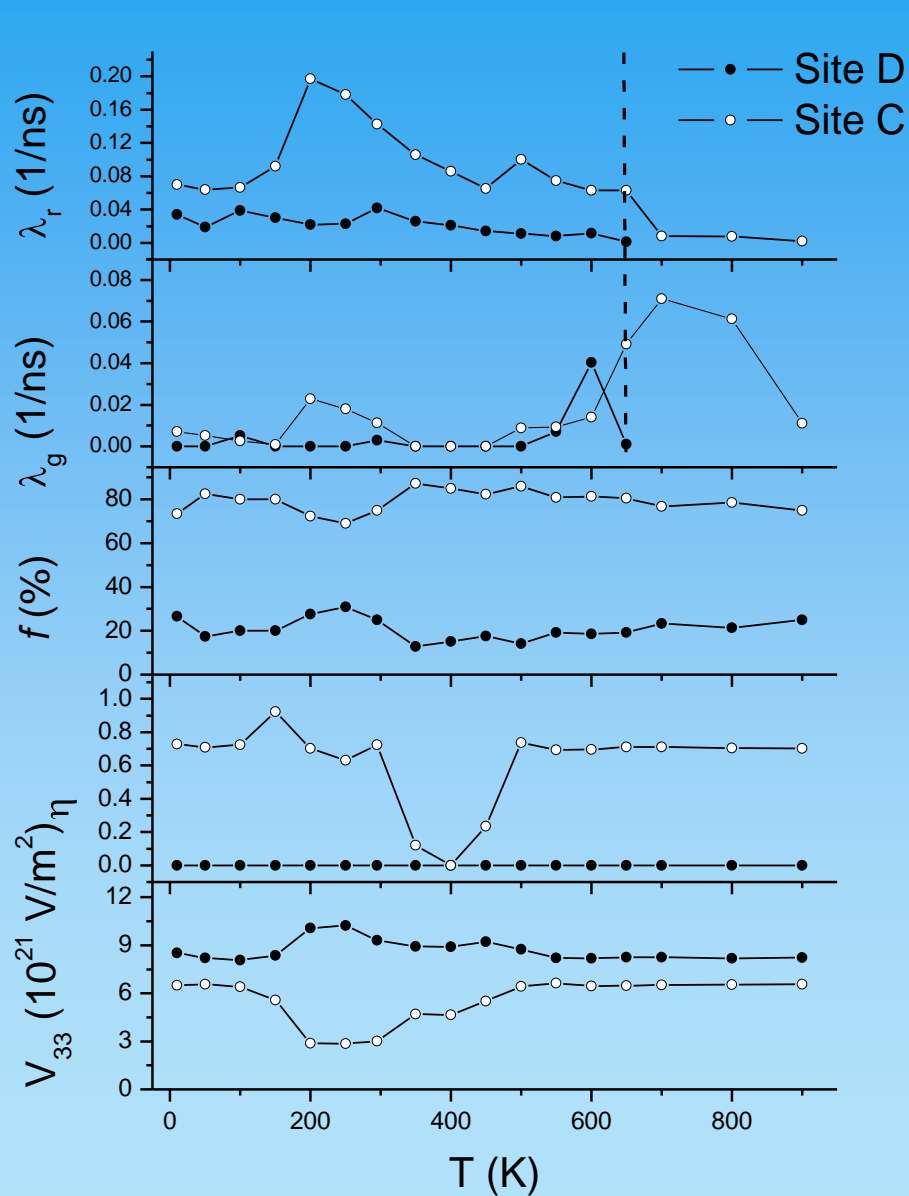
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FP-APW+lo results in pure Sc$_2$O$_3$

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[1] D. Richard, et al., PRB 82, 035206 (2010).

$[V_{33}]=10^{21}\ V/m^2;\ [d_{NN}]=Å$

Comparison between APW+lo results using experimental and refined structural parameters

Parameters	Aprox	Site D			Site C		
		d_{NN}	V_{33}	η	d_{NN}	V_{33}	η
Experimental	LDA	2.12	+4.53	0.00	2.08	-2.98	0.71
	CW	2.12	+4.52	0.00	2.08	-2.97	0.69
refined	LDA	2.12	+4.69	0.00	2.09	-3.11	0.53
	CW	2.12	+4.59	0.00	2.09	-2.92	0.52
PAC in ^{44}Sc results [1]			4.19(2)	0.00		2.741(7)	0.630(3)

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FP-APW+lo results in pure Sc_2O_3

η

0.70
0.69
0.01
0.00
-0.01

- Sitio D (filled circles)
- Sitio C (open circles)

V_{33} (10^{21} V/m^2)

4.8
4.7
4.6
4.5
4.4
-2.9
-3.0
-3.1
-3.2

E (Ry)

-28056
-28057
-28058

RKMAX: 5, 6, 7, 8, 9, 10

DOS (A. U.)

E_F

pure Sc_2O_3

O-2p

Sc-3d

Sc_2O_3:Cd - site D

Cd-4d acceptor state

Sc_2O_3:Cd - site C

Cd-4d

Energy (eV): -3, -2, -1, 0, 1, 2, 3, 4, 5

[1] D. Richard, et al., PRB 82, 035206 (2010).
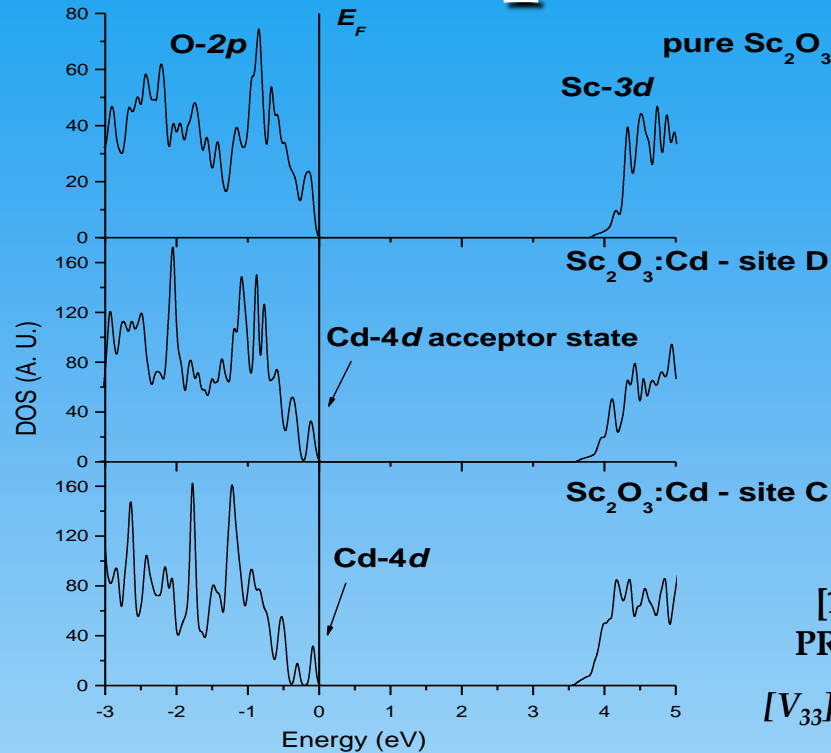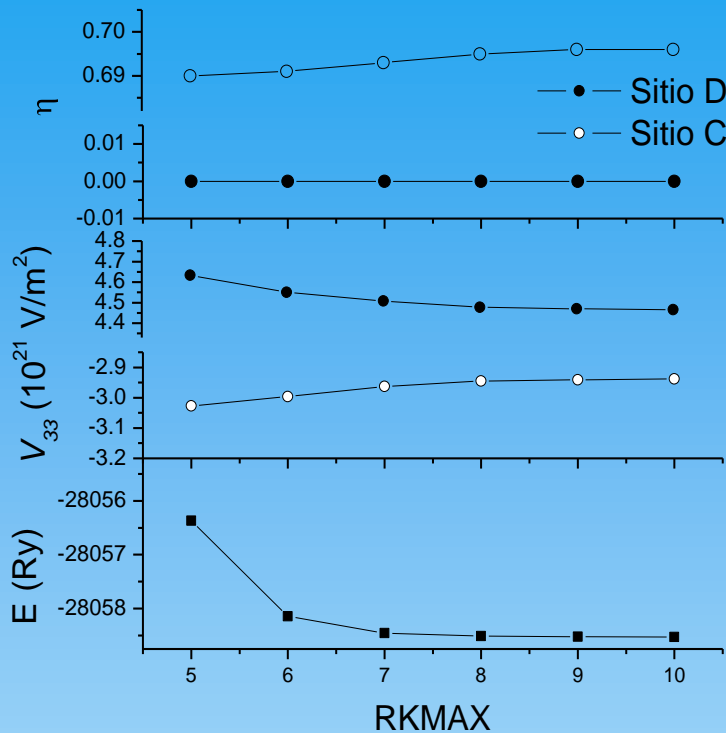
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PAC in ^{44}Sc results [1]		4.19(2)	0.00		2.741(7)	0.630(3)	

Total Density of States Sc$_2$O$_3$:Cd
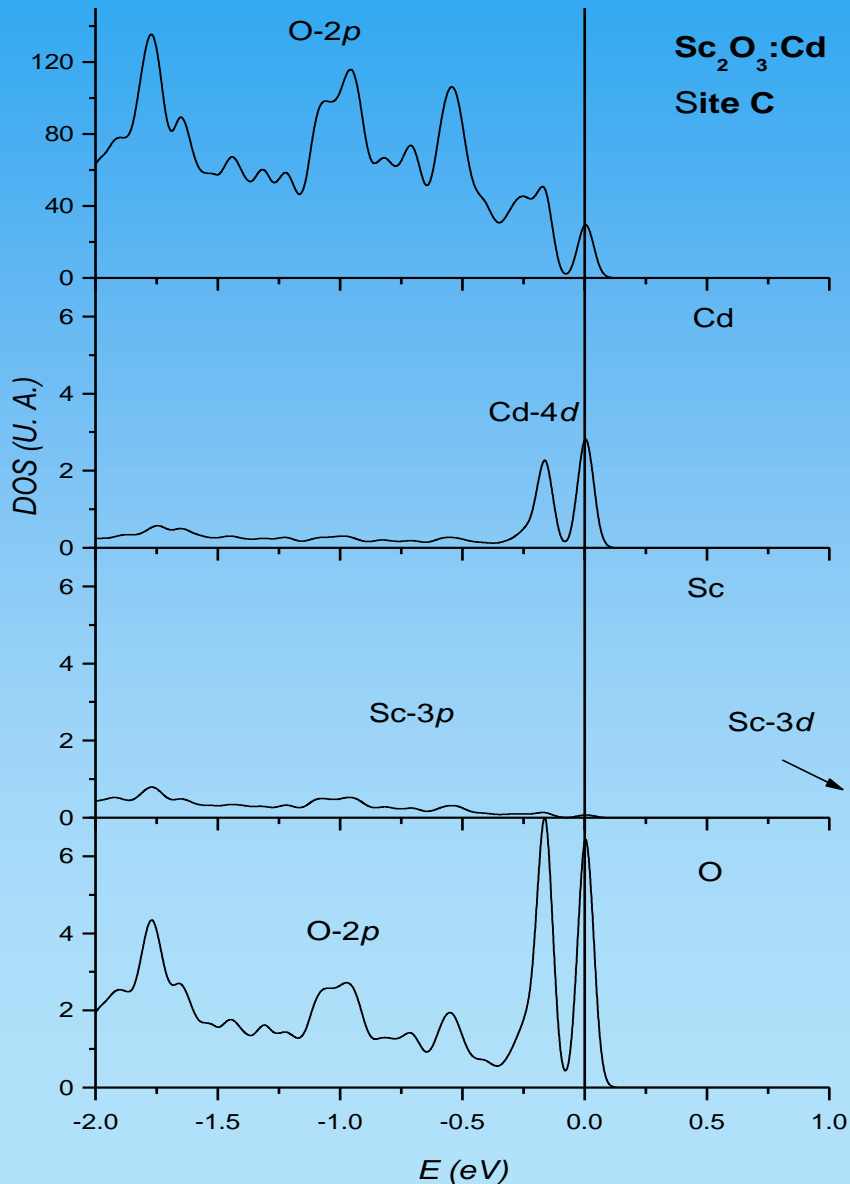
Neutral cell (Cd^0)

Total Density of States Sc₂O₃:Cd

Neutral cell (Cd⁰)

Charged cell (Cd⁻¹)

FP-APW+lo results in Cd-doped Sc$_2$O$_3$ for the unrelaxed and relaxed cell*

System	APW Approx.	Site D				Site C			
		d_{NN}	V_{33}	η	Dir. V_{33}	d_{NN}	V_{33}	η	Dir. V_{33}
Pure Sc2O3	LDA	2.12	4.63	0.0	[111]	2.08 2.12 2.16	-2.98	0.71	[0 -1 0.7]
Unrelaxed Sc$_2$O$_3$:Cd	LDA	2.12	8.65	0.0	[111]	2.08 2.12 2.16	-4.91	0.65	[0 -1 0.7]
Relaxed Sc$_2$O$_3$:Cd	LDA	2.28	8.05	0.0	[111]	2.17 2.30 2.31	6.75	0.74	[0 -0.9 1]
PAC results (T=900 K)		8.22$_1$	0.0	[111]	-	6.56$_1$	0.70$_1$	[0 -1 1]	

$[V_{33}] = 10^{21}$ V/m^2; $[d_{NN}] = $Å

* Cd-doped Sc$_2$O$_3$ results for the charged cell (Cd^{-1})

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FP-APW+lo results in Cd-doped Sc_2O_3 for the unrelaxed and relaxed cell*

System	APW Approx.	Site D				Site C			
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$[V_{33}]=10^{21}\ V/m^2;\ [d_{NN}]=Å$

* Cd-doped Sc_2O_3 results for the charged cell (Cd^{-1})

EFG dependence of the charge state of the Cd impurity

Cell Charge State	APW Approx.	Site D				Site C			
		d_{NN}	V_{33}	η	Dir. V_{33}	d_{NN}	V_{33}	η	Dir. V_{33}
Uncharged Cell	WC	2.22	+8.24	0.00	[111]	2.10 2.24 2.32	+3.06	0.64	[0 0 1]
Neutral Cell	WC	2.25	+8.32	0.00	[111]	2.14 2.28 2.32	-3.81	0.34	[0 -0.7 1]
Charged Cell	WC	2.28	+8.16	0.00	[111]	2.19 2.31 2.32	+6.50	0.71	[0 -0.8 1]

These results were checked with the others approximations, LDA and GGA

$[V_{33}]=10^{21}$ V/m^2; $[d_{NN}]=$Å

Uncharged cell (Cd^{+1}): 1 removed electron in the cell

Neutral cell (Cd^0): neutral Cd atom

Charged cell (Cd^{-1}): 1 added electron in the cell

EFG dependence of the charge state of the Cd impurity

Cell Charge State	APW Approx.	Site D				Site C			
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EFG contributions

	Uncharged Cell			Neutral Cell			Charged Cell		
Cd at D site									
	V_{11}	V_{22}	V_{33}	V_{11}	V_{22}	V_{33}	V_{11}	V_{22}	V_{33}
p	-3.34	-3.34	**6.68**	-3.18	-3.18	**6.36**	-3.00	-3.00	**6.00**
d	-0.89	-0.89	**1.78**	-1.08	-1.08	**2.16**	-1.17	-1.17	**2.35**
s-d	0.10	0.10	-0.20	0.10	0.10	-0.20	0.10	0.10	-0.20
total	-4.13	-4.13	**8.26**	-4.16	-4.16	**8.32**	-4.07	-4.07	**8.15**

$[V_{ii}] = 10^{21}$ *V/m²*

EFG contributions

	Uncharged Cell			Neutral Cell			Charged Cell		
Cd at D site									
	V_{11}	V_{22}	V_{33}	V_{11}	V_{22}	V_{33}	V_{11}	V_{22}	V_{33}
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total	-4.13	-4.13	**8.26**	-4.16	-4.16	**8.32**	-4.07	-4.07	**8.15**

$[V_{ii}]=10^{21}\ V/m^2$

EFG contributions

Cd at D site

	Uncharged Cell			Neutral Cell			Charged Cell		
	V_{11}	V_{22}	V_{33}	V_{11}	V_{22}	V_{33}	V_{11}	V_{22}	V_{33}
p	-3.34	-3.34	**6.68**	-3.18	-3.18	**6.36**	-3.00	-3.00	**6.00**
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s-d	0.10	0.10	-0.20	0.10	0.10	-0.20	0.10	0.10	-0.20
total	-4.13	-4.13	**8.26**	-4.16	-4.16	**8.32**	-4.07	-4.07	**8.15**

Cd at C site

	Uncharged Cell			Neutral Cell			Charged Cell		
	V_{11}	V_{22}	V_{33}	V_{11}	V_{22}	V_{33}	V_{11}	V_{22}	V_{33}
p	9.60	-6.47	**-3.12**	-2.24	7.46	**-5.22**	-1.20	-3.67	**4.87**
d	-10.32	4.20	**6.12**	3.46	-4.86	**1.39**	0.25	-2.03	**1.78**
s-d	0.17	-0.21	0.05	0.04	0.15	-0.19	0.02	0.13	-0.15
total	-0.5	-2.53	**3.03**	1.25	2.57	**-3.82**	-0.93	-5.57	**6.50**

$[V_{ii}] = 10^{21}$ V/m²

EFG contributions

Cd at D site

	Uncharged Cell			Neutral Cell			Charged Cell		
	V_{11}	V_{22}	V_{33}	V_{11}	V_{22}	V_{33}	V_{11}	V_{22}	V_{33}
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s-d	0.10	0.10	-0.20	0.10	0.10	-0.20	0.10	0.10	-0.20
total	-4.13	-4.13	**8.26**	-4.16	-4.16	**8.32**	-4.07	-4.07	**8.15**

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p	9.60	-6.47	**-3.12**	-2.24	7.46	**-5.22**	-1.20	-3.67	**4.87**
d	-10.32	4.20	**6.12**	3.46	-4.86	**1.39**	0.25	-2.03	**1.78**
s-d	0.17	-0.21	0.05	0.04	0.15	-0.19	0.02	0.13	-0.15
total	-0.5	-2.53	**3.03**	1.25	2.57	**-3.82**	-0.93	-5.57	**6.50**

$[V_{ii}]=10^{21}$ V/m^2

Partial Density of States Cd-4*d*
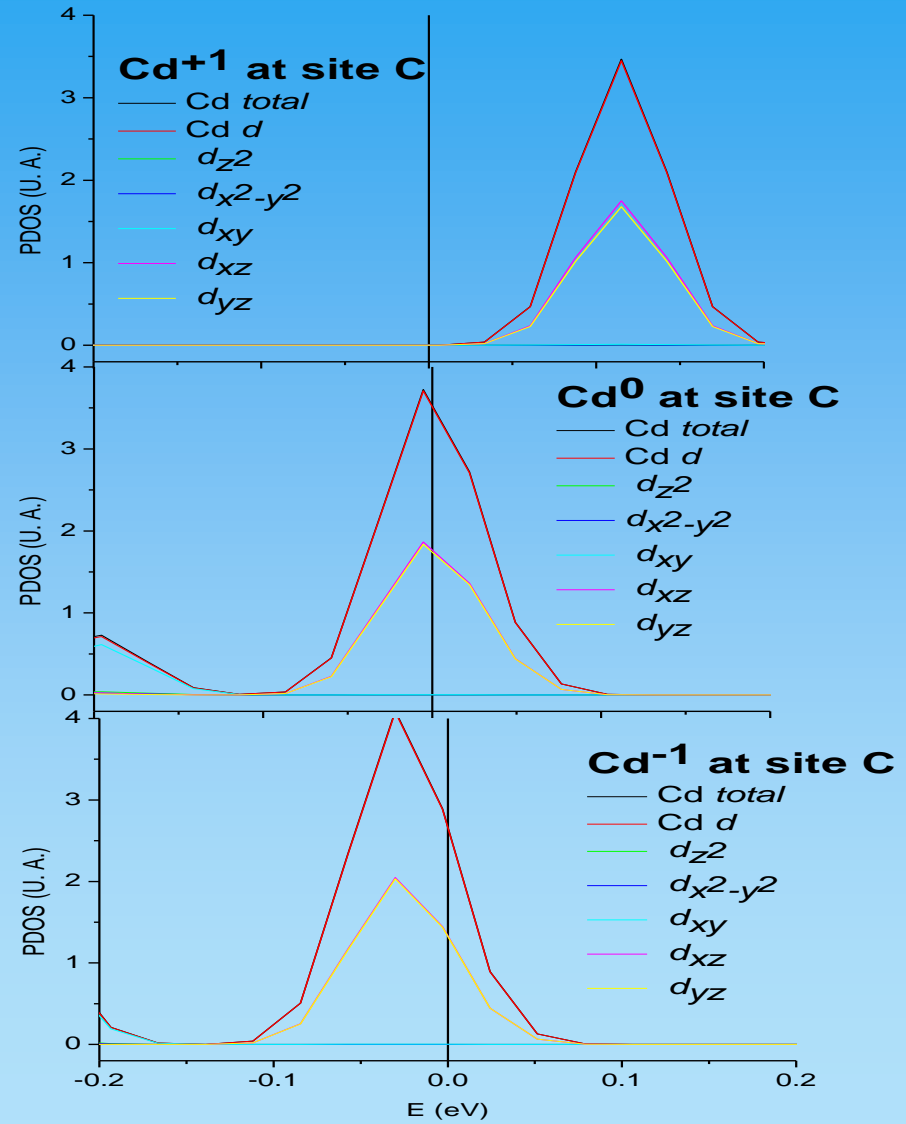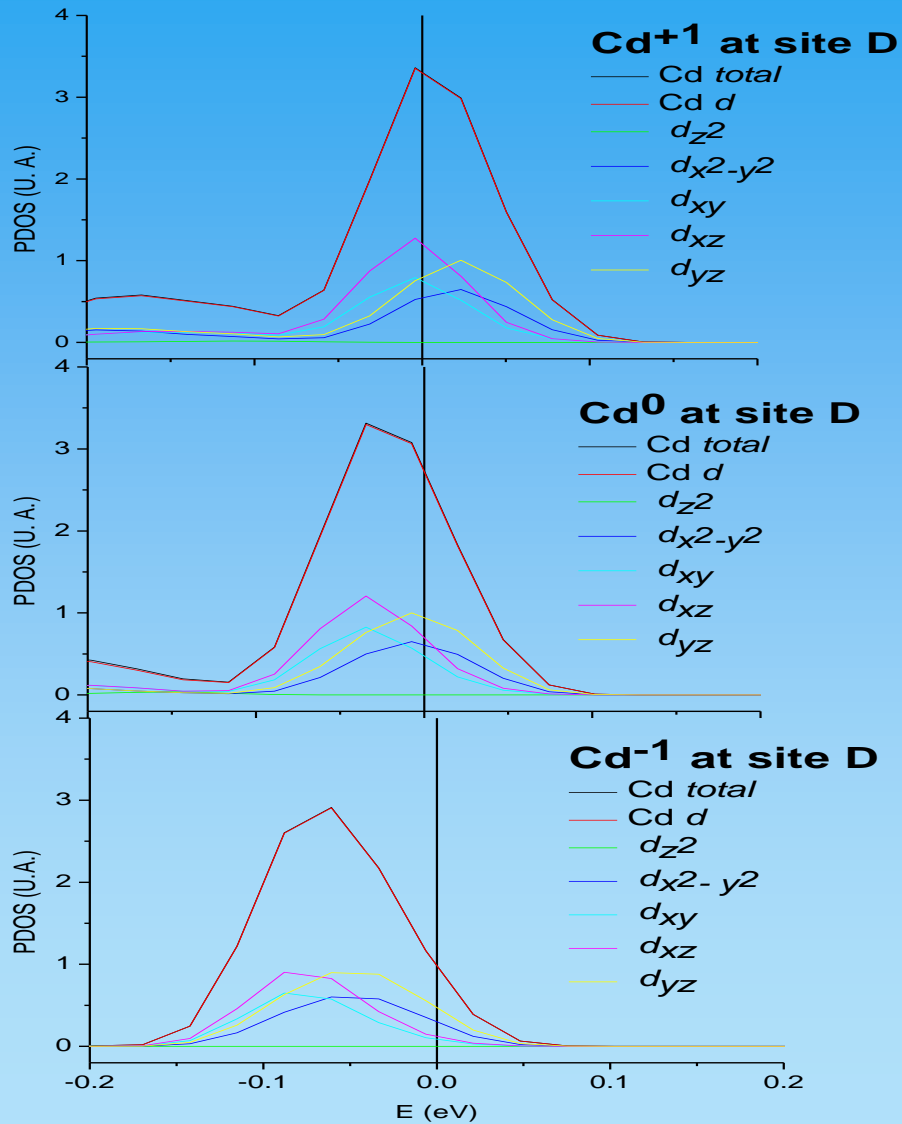
Comparison of the results
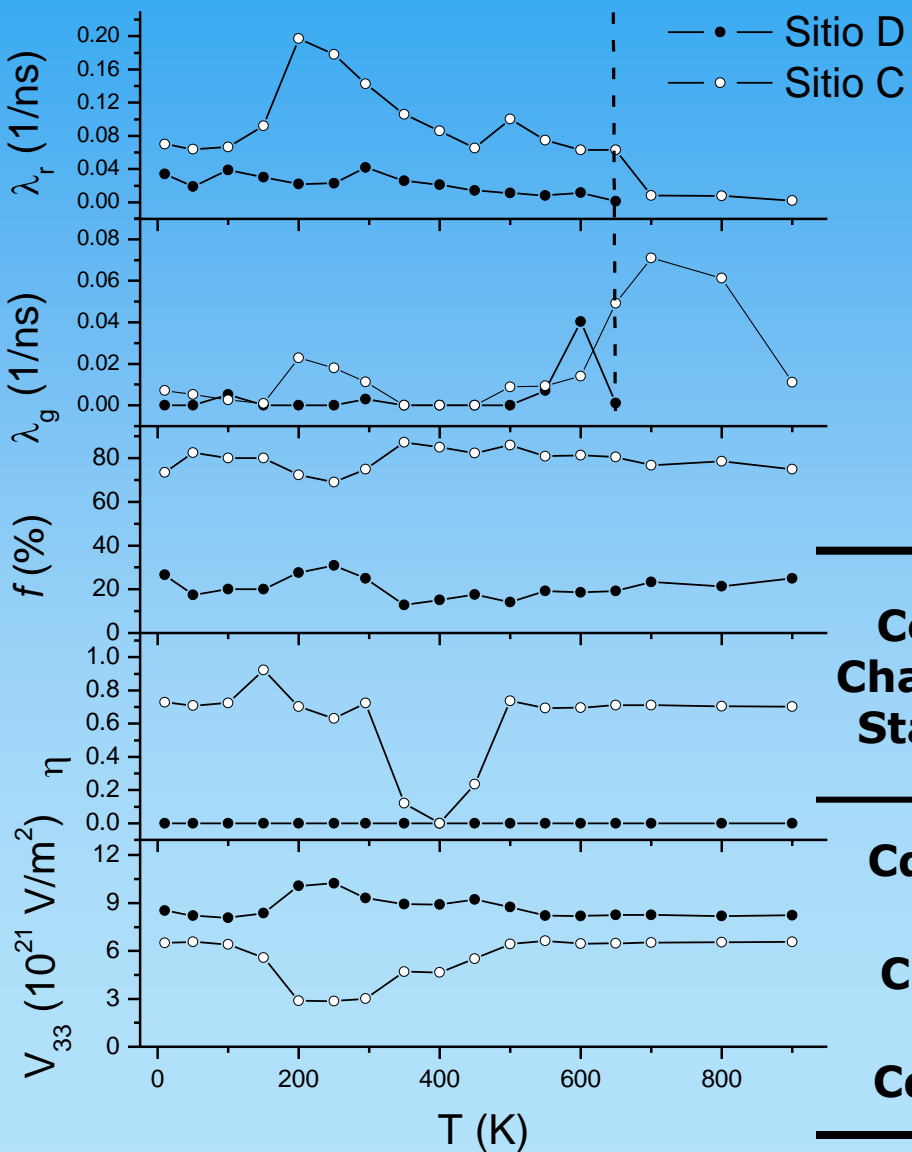
Cell Charge State	APW Approx.	Site D		Site C	
		V_{33}	η	V_{33}	η
Cd^{+1}	WC-GGA	+8.24	0.00	+3.06	0.64
Cd^0	WC-GGA	+8.32	0.00	-3.81	0.34
Cd^{-1}	WC-GGA	+8.16	0.00	+6.50	0.71

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Comparison of the results

> ➤ EFG calculated in Cd at site D does not present charge state dependence.

> ➤ EFG in Cd at site C has a strong charge state dependence.

> ➤ The Abragam and Pound constant at site C is larger of that of site D in all the temperature range.
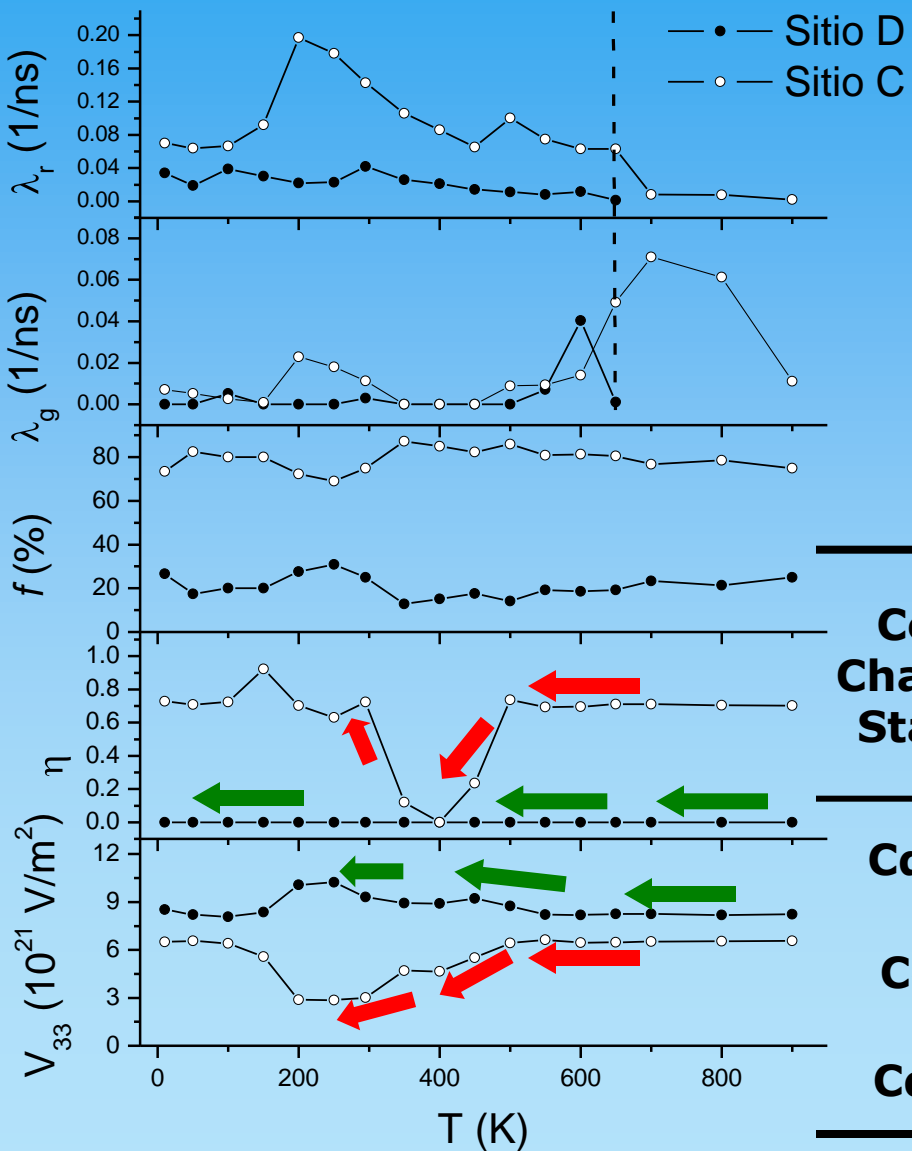
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Outline

- Studied system

- PAC technique

- Experimental results

- FP-APW+lo calculations

- **Final remarks**

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➤ From this experimental and *ab initio* approach, we can conclude that the dynamic interaction observed at Cd impurities located at C sites is more intense than the dynamic interaction at the D site. These behavior of the EFG is attributed to the symmetry of the each site.

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➢ We can see that the increase of the EFG dependence with the charge state of the impurity is correlated with an increase of the strength of the dynamic interaction.

➢ Finally, we conclude that an *ab initio* study can help to understand the underlying physics described by the phenomenological Abragam and Pound model.
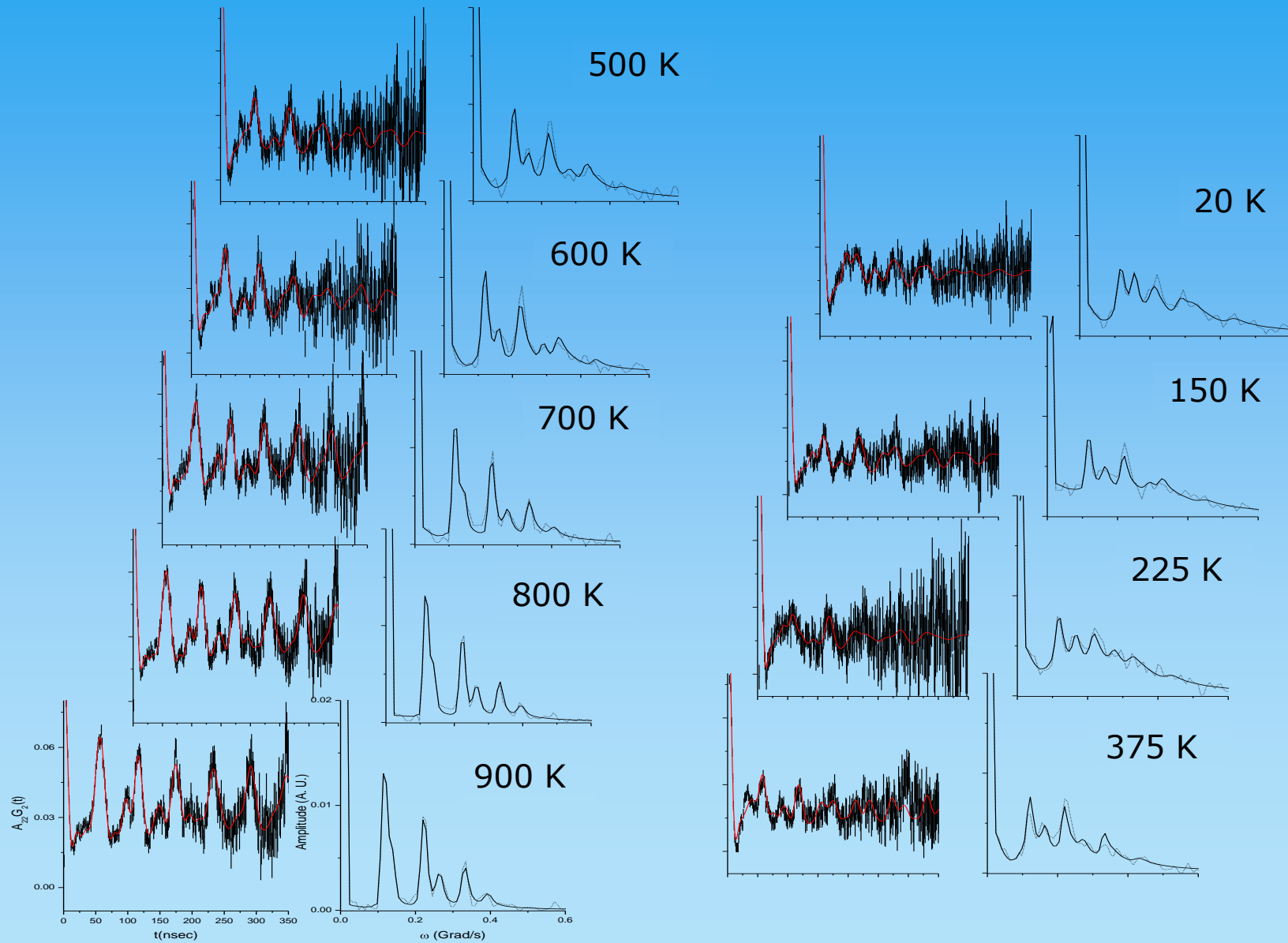
Cd- doped In$_2$O$_3$
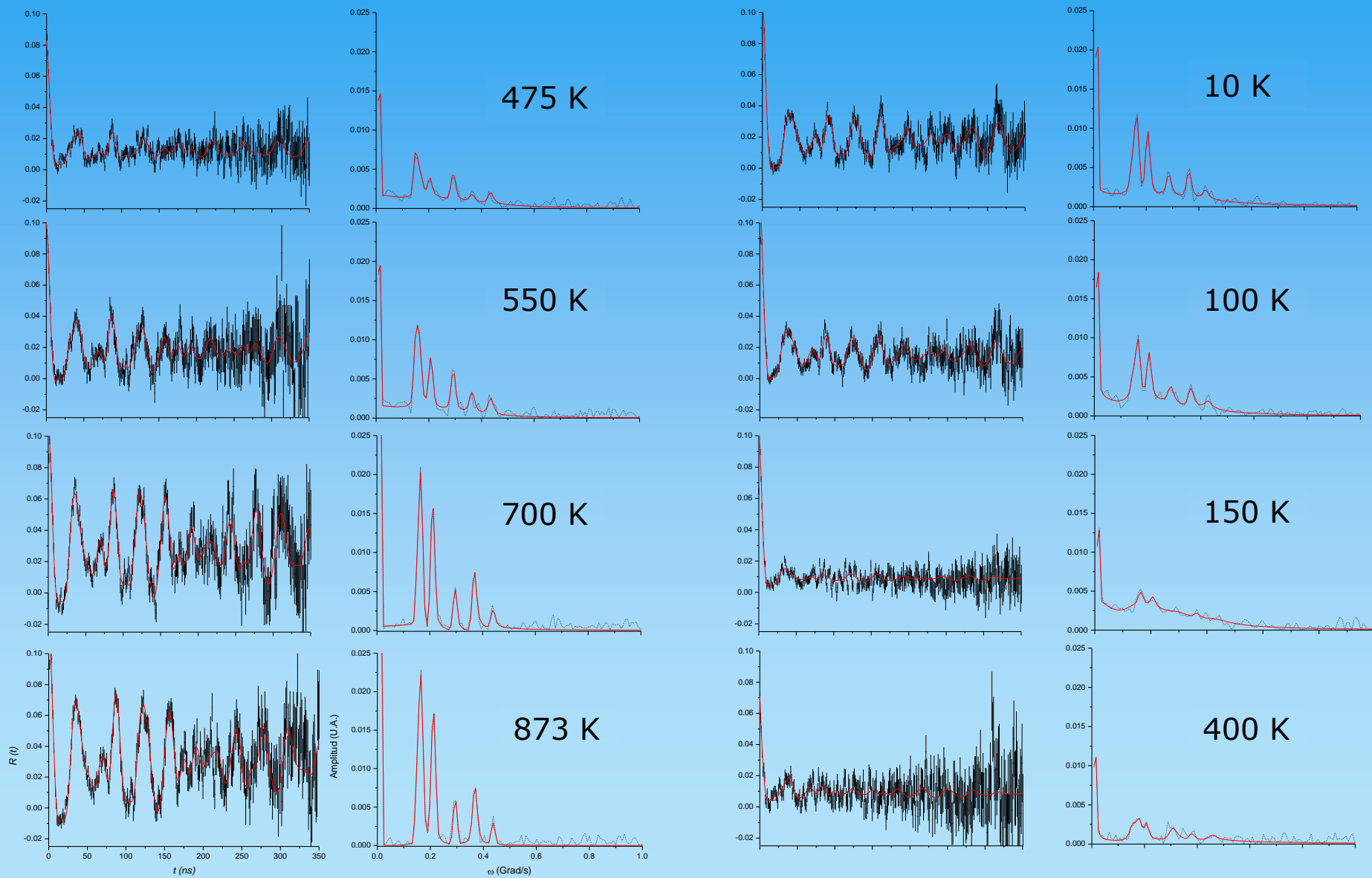
In$_2$O$_3$:Cd – HFIs vs. T
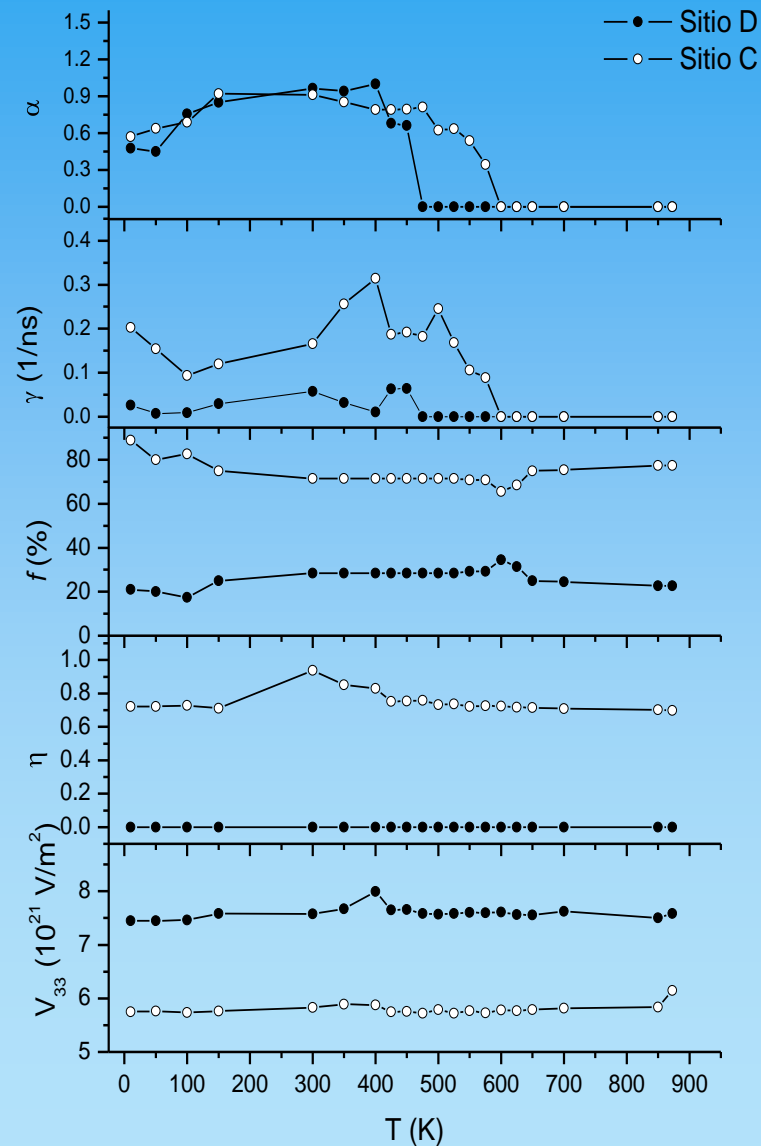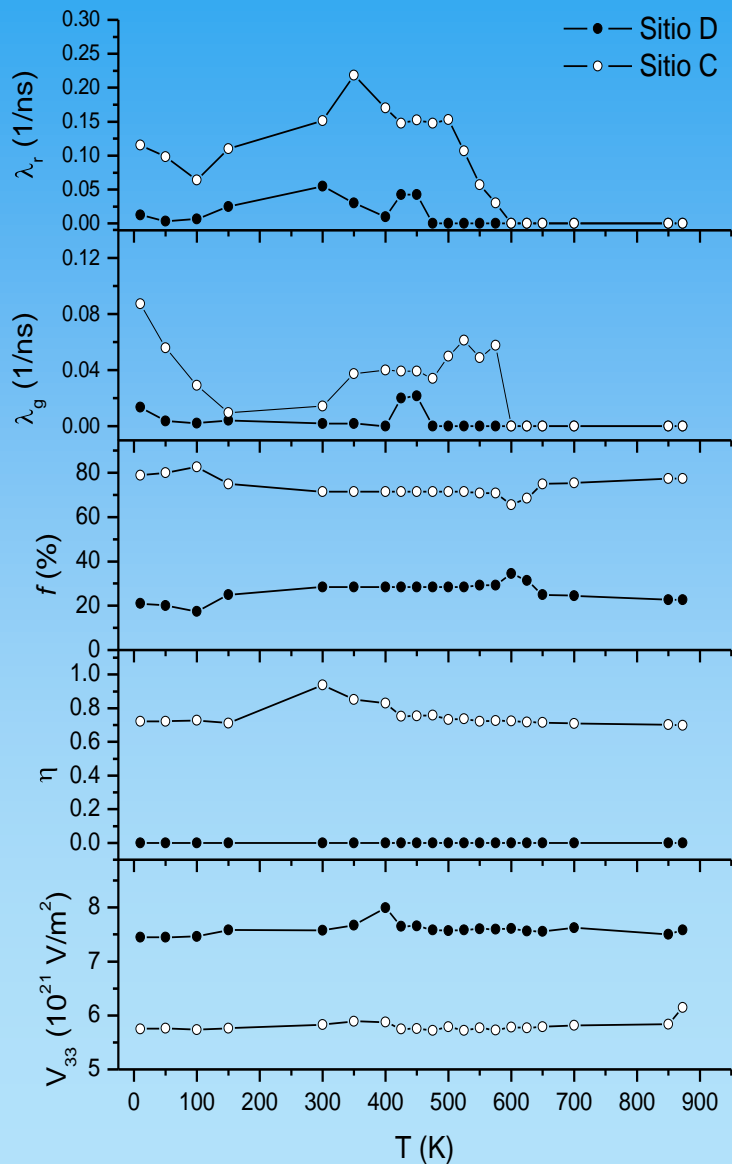
Cd-doped SnO

Charge state	Aprox.	d_{NN} (Å)	h	V_{33} (10^{21}V/m^2)	
Descargada	LDA	2.257	0.000	+7.79	← HFI2
Neutra	LDA	2.266	0.000	+5.26	← HFI1
Cargada	LDA	2.368	0.000	-4.52	