Ab initio molecular dynamics of CdTe oxides

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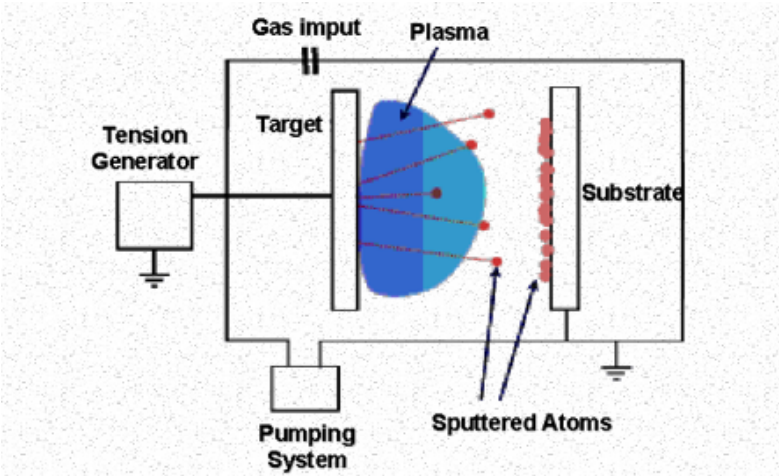
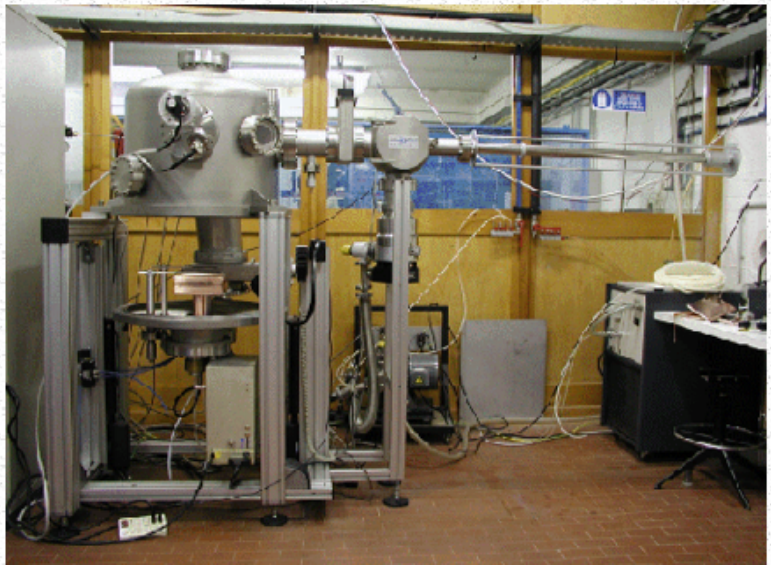
Abdus Salam International Centre for Theoretical Physics.

Introduction

- CdTe:O thin films grown by *r.f. sputtering*.
- Possible windows material for CdTe/CdS solar cells..
- In-doped $CdTeO_3$ is a transparent conducting oxide.
- Cd_3TeO_6 is $n-$type semiconductor.
- The amorphous order is a challenge for understanding the material.

R.f. sputtering





Material

Table 1
Sample deposition parameters

Sample	Pressure (mbar)			Power (mW cm^{-2})	Target bias (V)
	O_2	N_2	Ar		
X10A1 [a]	4.0×10^{-5}	1.6×10^{-4}	9.8×10^{-3}	159	−600
X11A1 [a]	4.0×10^{-5}	1.6×10^{-4}	9.8×10^{-3}	159	−600
X11A2	4.0×10^{-5}	9.6×10^{-4}	9.0×10^{-3}	159	−600
X11A3	4.0×10^{-5}	5.0×10^{-3}	5.0×10^{-3}	159	−600
X11A4 [b]	4.0×10^{-5}	9.9×10^{-3}	$\cong 0$	159	−600
X11G1 [a]	4.0×10^{-5}	1.6×10^{-4}	9.8×10^{-3}	159	−600
X11G3 [a]	4.0×10^{-5}	1.6×10^{-4}	9.8×10^{-3}	159	−600
X11G4 [a]	4.0×10^{-5}	1.6×10^{-4}	9.8×10^{-3}	159	−600

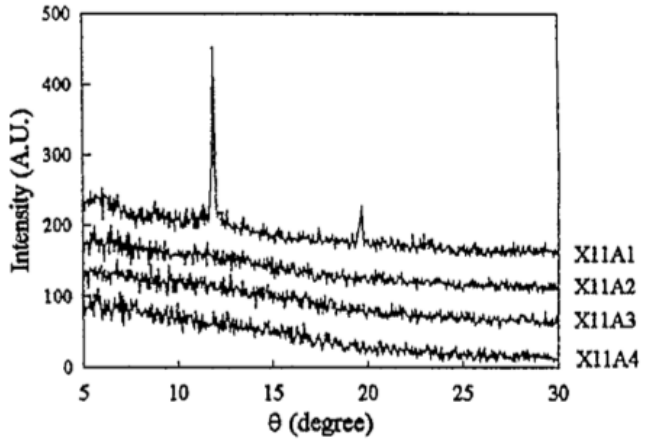
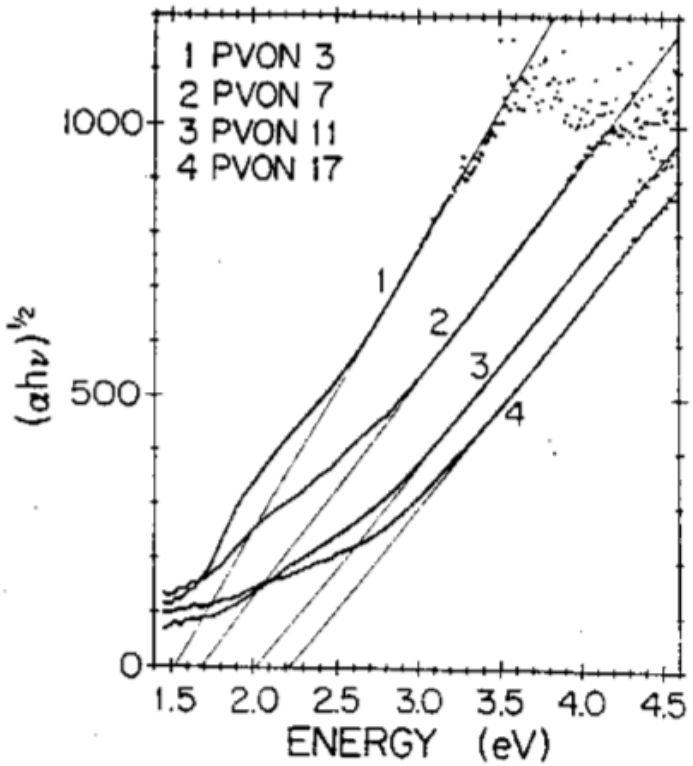
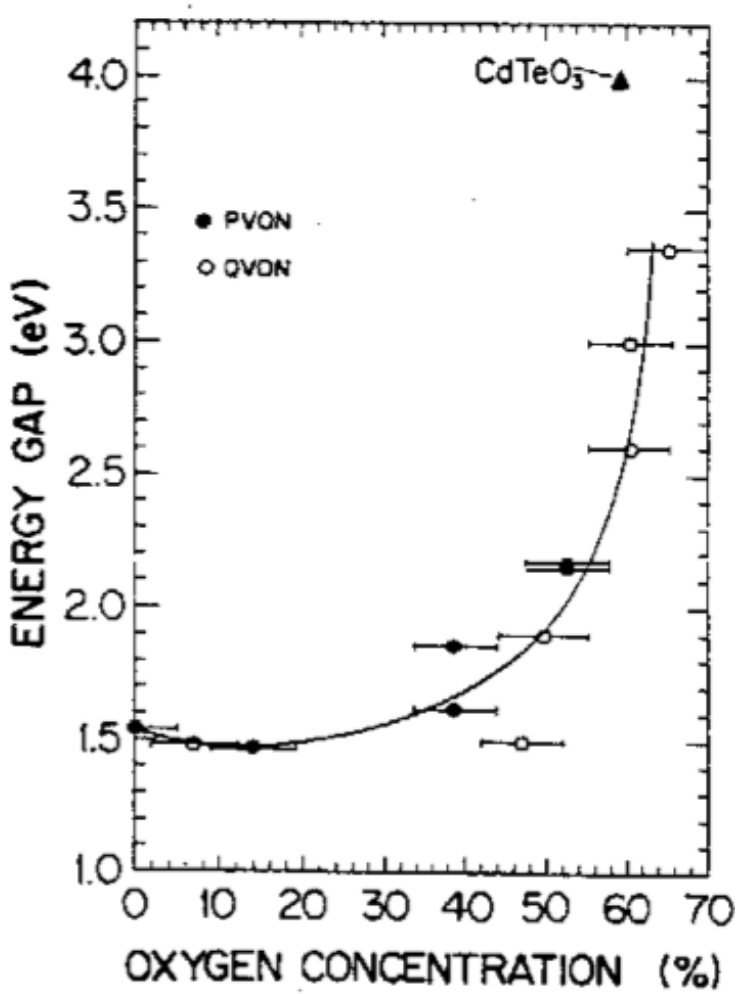


Fig. 1. X-ray diffraction patterns for some representative CdTe:O samples.

X-ray diffraction. M.Y. El Azhari et al., Thin Solid Films **295**, 131 (1997).

Optical properties

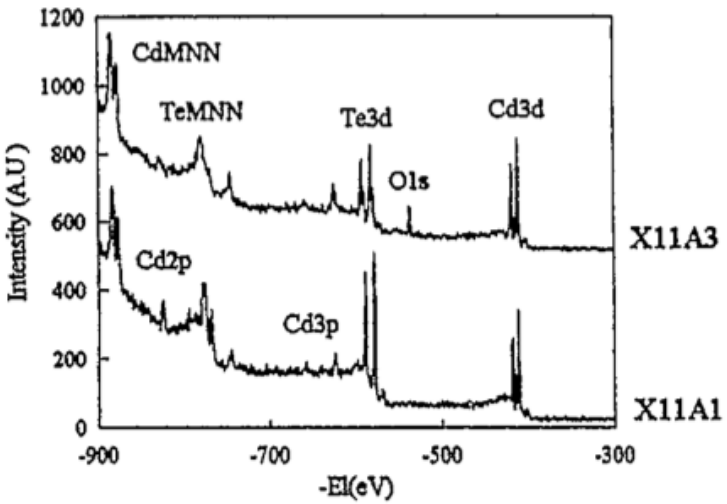


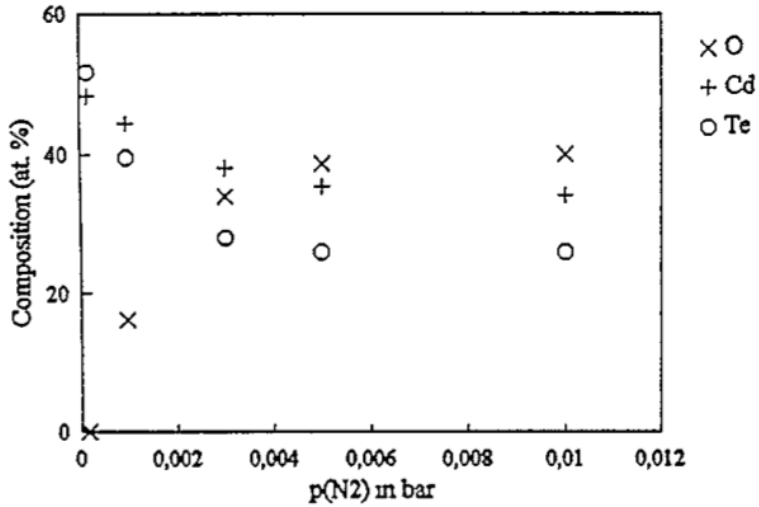


Optical gap vs oxygen content. Espinoza et al, J. Vac. Sci. Technol. A **11**, 3062 (1993).

XPS

$$\frac{N(\mathrm{Te})}{N(\mathrm{Cd})} = \frac{\sigma(\mathrm{Cd}\ 3d_{5/2})}{\sigma(\mathrm{Te}\ 3d_{5/2})} \frac{I(\mathrm{Te}\ 3d_{5/2})}{I(\mathrm{Cd}\ 3d_{5/2})}$$





$$\frac{N(\mathrm{O})}{N(\mathrm{Cd})} = \frac{\sigma(\mathrm{Cd}\ 3d_{5/2})}{\sigma(\mathrm{O}\ 1s)} \frac{I(\mathrm{O}\ 1s)}{I(\mathrm{Cd}\ 3d_{5/2})}$$

$$N(\mathrm{Cd}) + N(\mathrm{Te}) + N(\mathrm{O}) = 100\%$$

Quantifying composition. M.Y. El Azhari et al. /Thin Solid Films **295**, 131 (1997).

Goal

To produce structural models of $CdTeO_x$.
Tool: *ab initio* molecular dynamics.

Statistical mechanics

The observed magnitudes in a macroscopical system are the average of these magnitudes in the ensemble of microstates compatible witht eh macrostate.

Microestado:

$$\Gamma = \{\vec{r}_1, \vec{r}_2, ..., \vec{r}_N, \vec{p}_1, \vec{p}_2, ..., \vec{p}_N\}$$

Macroestado: P, V, T, $\vec{M}$.

Magnitud macroscópica observada

$$A_{obs} = \langle A \rangle = \frac{\sum_\Gamma A(\Gamma)}{\sum_\Gamma 1} = \sum_\Gamma P(\Gamma) A(\Gamma).$$

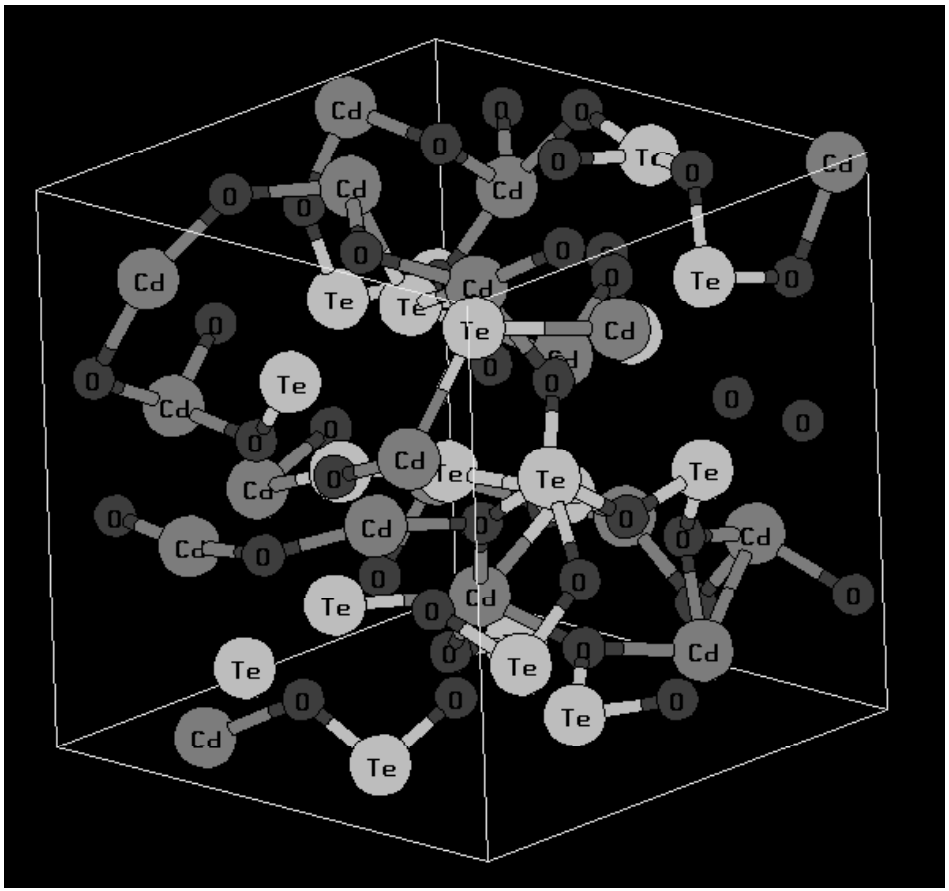
Molecular dynamics

It is a method to generate a sequence of microstates $\{\Gamma_n\}$. It is based on the Newton equations:.

$$\frac{d^2\vec{r}_i}{dt} = \frac{\vec{f}_i}{m_i}.$$

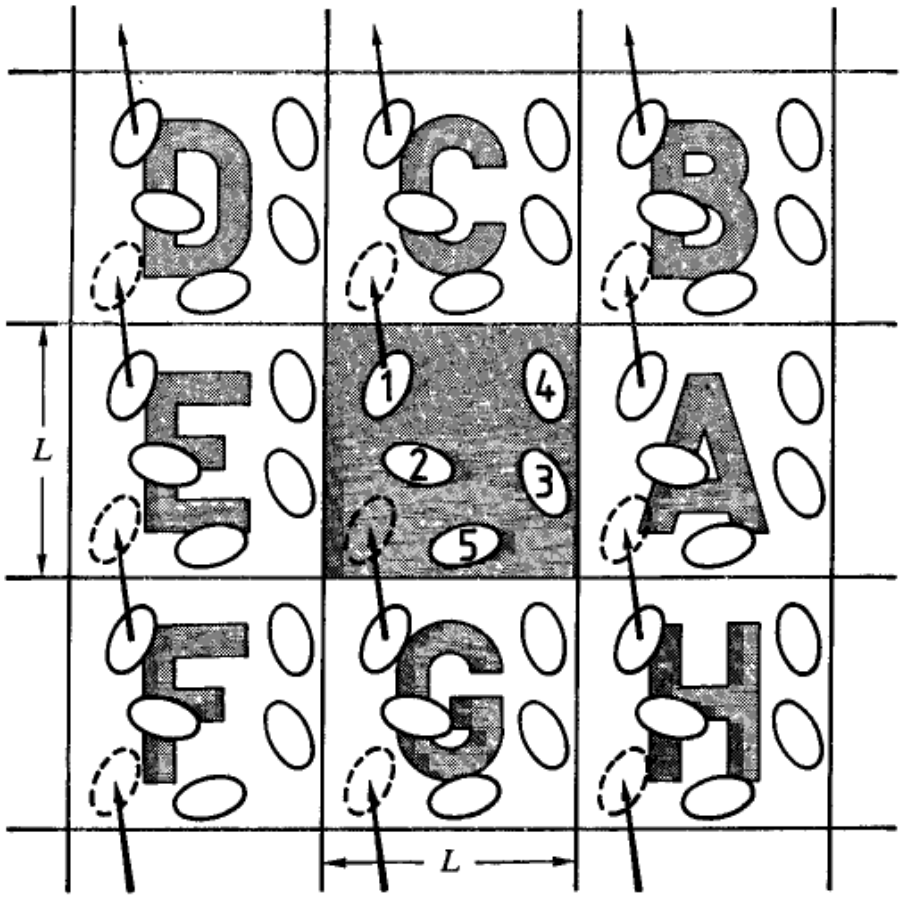
Solved by finite difference methods..

Our system



Snapshot of a configuration of CdTeO. Periodical boundary conditions..

Periodic boundary conditions



Verlet algorithm

$$\vec{r}(t+\Delta t) = 2\vec{r}(t) - \vec{r}(t-\Delta t) + (\Delta t)^2 \vec{a}(t), \qquad \vec{a} = \frac{\vec{f}}{m}.$$

The velocities, if needed to calculate a property, can be obtained from

$$\vec{v}(t) = \frac{\vec{r}(t+\Delta t) - \vec{r}(t-\Delta t)}{2\Delta t}$$

¿How to calculate the forces?

- Empirical force-fields.
- Quantum mechanics (our choice).

Density Functional Theory

Is an approximate solution to the real problem of finding the electronic density in a multielectron system.

$$(-\nabla^2 + V_{eff})|\phi_i\rangle = \epsilon_i|\phi\rangle, \quad n(\mathbf{r}) = \sum_i |\phi_i(\mathbf{r})|^2$$

$$V_{eff}(\mathbf{r}) = V_{ext}(\mathbf{r}) + \int dr' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + v_{xc}(\mathbf{r})$$

$n(\mathbf{r}) \Longrightarrow$ Energy, forces, stress tensor, ...

Exchange-correlation potential $v_{xc}(r) = \frac{\delta E_{xc}}{\delta n} = \frac{\partial}{\partial n}(n e_{xc}(n))\Big|_{n=n(r)}$

Example: LDA

$$
\begin{aligned}
E_{xc}^{LDA}[n] &= \int e_{xc}[n(r)]\, n(r)\, d^3r, \\
v_{xc}(r) &= \frac{\delta E_{xc}^{LDA}}{\delta n} = \frac{\partial}{\partial n}(n e_{xc}(n))\Big|_{n=n(r)} \\
e_{xc}(n) &= e_x^{\mathrm{hom}}(n) + e_c^{\mathrm{hom}}(n), \\
e_x^{\mathrm{hom}}(n) &= -(81/64\pi)^{1/3} n^{1/3},
\end{aligned}
$$

e_c^{hom} is a function fitted to QMC results for the homogeneous electron gas

$$
e_c^{\mathrm{hom}}(n) = \begin{cases} -0.14231(1 + 1.0529\sqrt{r_s} + 0.3334 r_s)^{-1}, r_s \geq 1 \\ -0.0480 + 0.0311 \ln r_s - 0.0116 r_s + 0.002 r_s \ln r_s, r_s < 1 \end{cases}
$$

$$
n = \left(\frac{4}{3}\pi r_s^3\right)^{-1}, \qquad r_s = \left(\frac{4}{3}\pi n\right)^{-1/3}
$$

Hellman-Feynman forces

$$\vec{F}_I = -\int n(\vec{r}) \frac{\partial V_{ext}}{\partial \vec{R}_I}\, d^3\vec{r} - \frac{\partial E_{II}}{\partial \vec{R}_I} + \vec{F}_{correc}. \qquad (1)$$

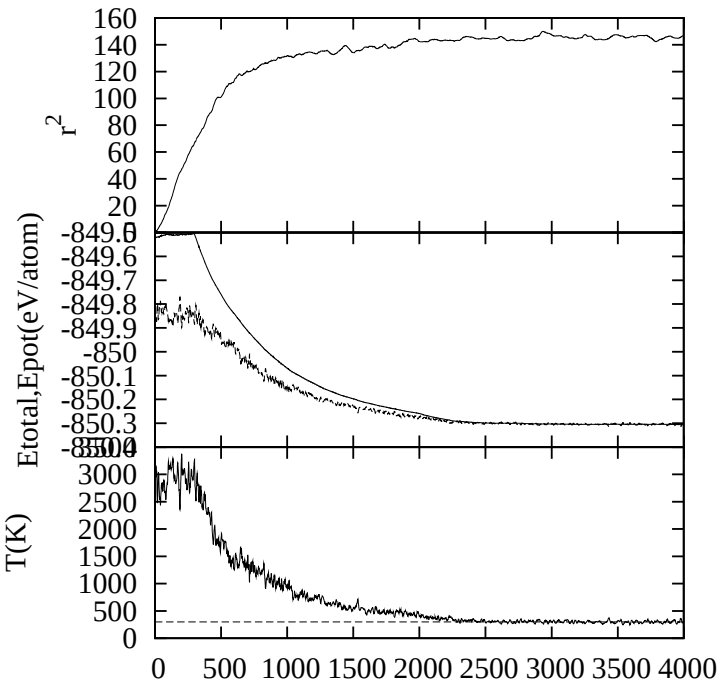
$$\begin{aligned} \vec{F}_{correc} &= -2\mathrm{Re}\sum_i \int \frac{\partial \psi_i^*}{\partial \vec{R}_I} \left[-\frac{1}{2}\nabla^2 + V_{KS} - \varepsilon_i \right] \psi_i \, d^3\vec{r} \\ &\quad - \int \left[V_{KS} - V^{in} \right] \, d^3\vec{r} \end{aligned}$$

Computational details

- Ultrasoft type with scalar relativistic effects.
- Cutoffs: 30 Ry for wavefunctions, 180 Ry for the charge density.
- Γ point sampling.
- Fermi smearing of 0.02 Ry.
- E_{xc} of Perdew, Burke and Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996).
- Stress tensor as Nielsen and Martin, Phys. Rev. Lett. 50, 697, 1983
- Implemented in Quantum-ESPRESSO.

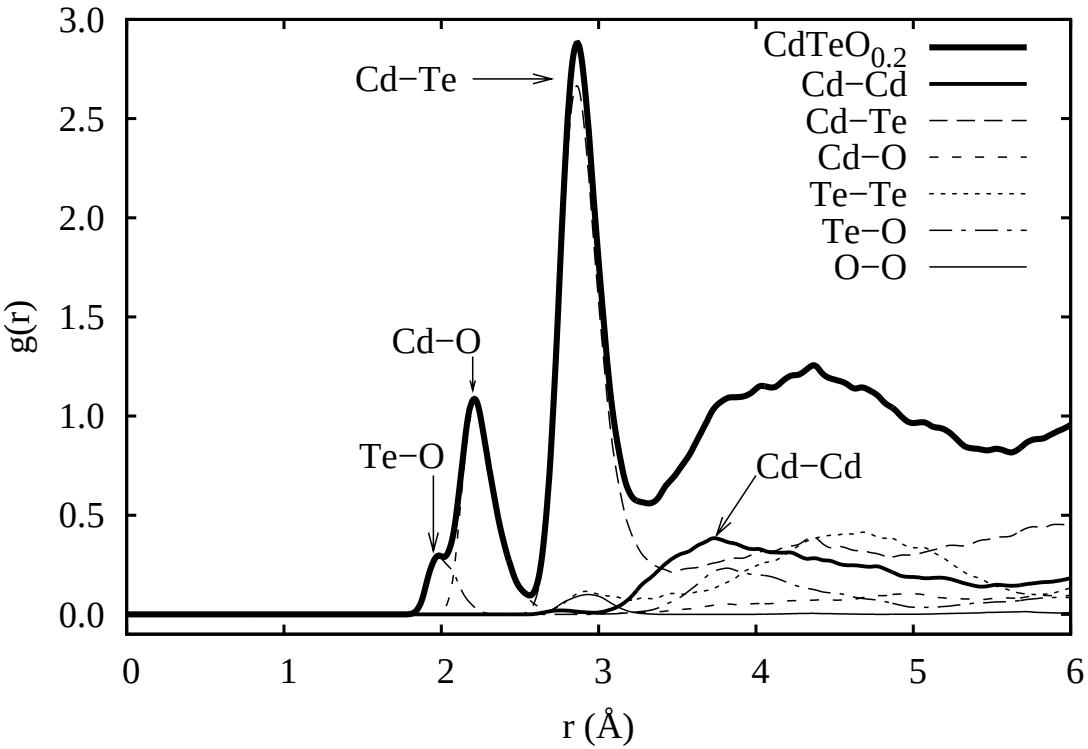
Sample preparation

MyPWSCF/CdTeO0.2/MD-PW/3000K/Scaling/Altix



- Define supercell: volume, atoms, random initial positions.
- Heat to 3000 K rescaling velocities (3-5 ps).
- Slow annealing to 300 K using Berendsen's algorithm $v' = v \times \sqrt{1 + (T/T_i - 1)\Delta t/\tau}$. Equilibration achieved in 15-20 ps.
- Once T and E_{total} are stable, sample during last 6 ps.

Analysis ($CdTeO_{0.2}$) (I)



$$g(r) = \frac{V}{N^2}\sum_{i,j}^{N}\langle\delta(r-r_{ij})\rangle,$$

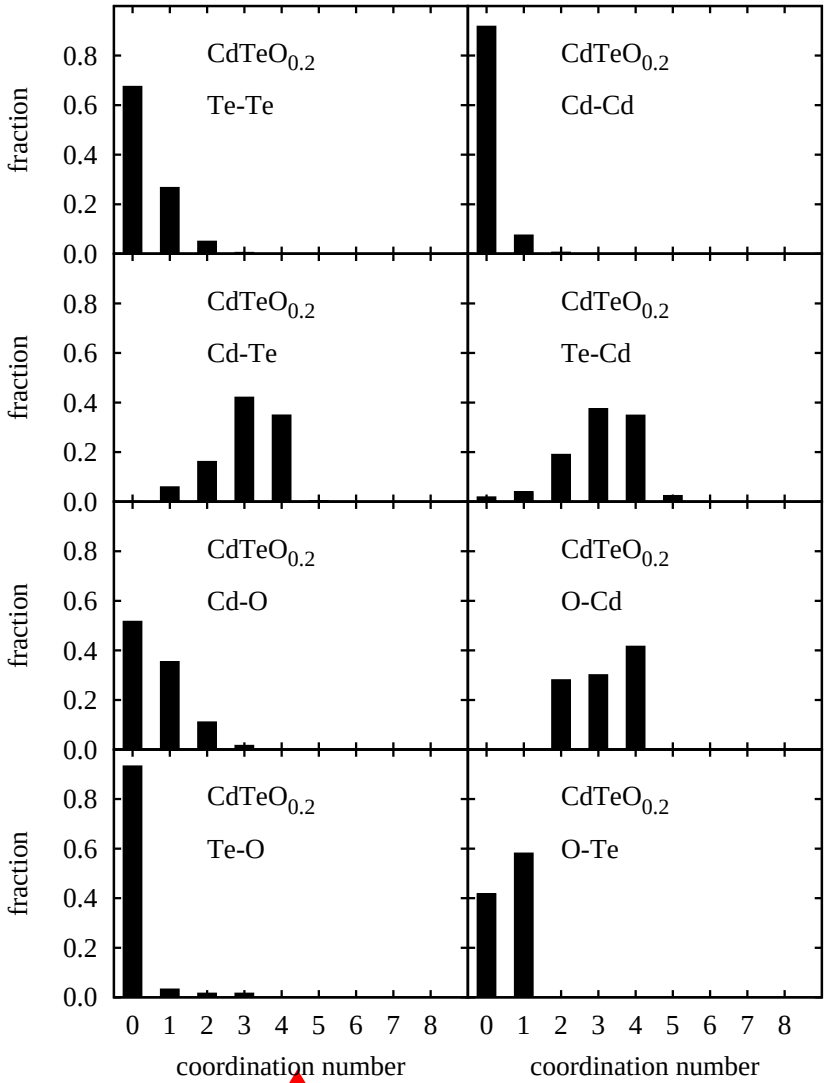
$$g_{ij}(r) = \frac{V}{N_i N_j}\sum_{k}^{N_i}\sum_{l}^{N_j}\langle\delta(r-r_{kl})\rangle.$$

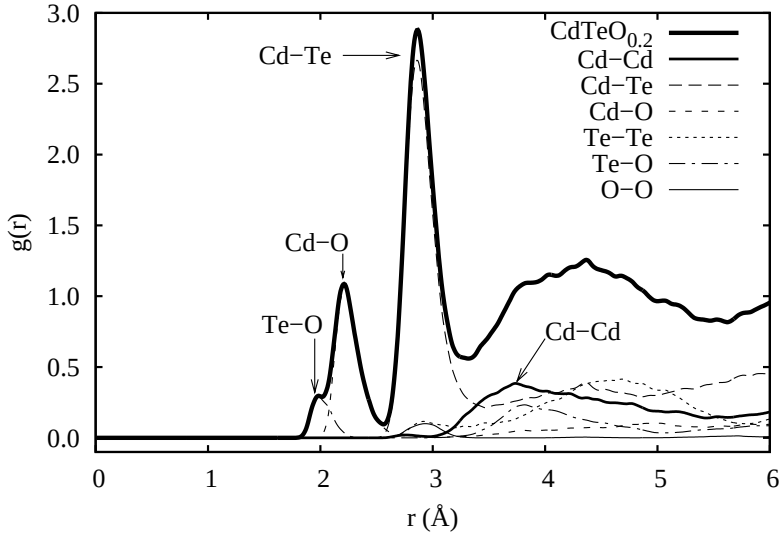
Total and partial pair distribution functions.

Calculated with Fumody.

http://www.gnm.cl/software/index.php/Fumody

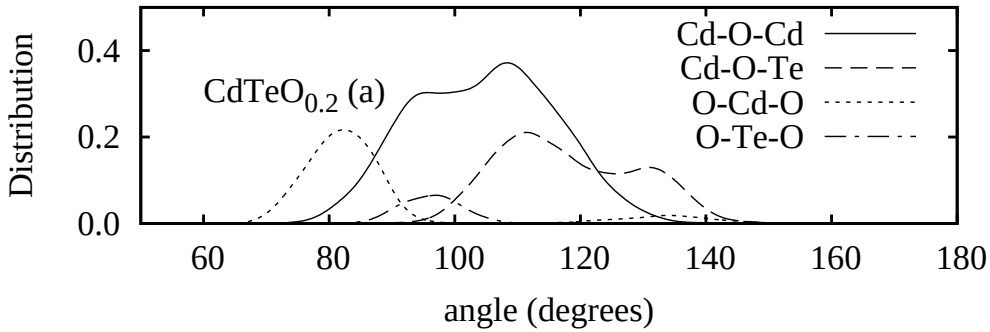
Analysis ($CdTeO_{0.2}$) (II)

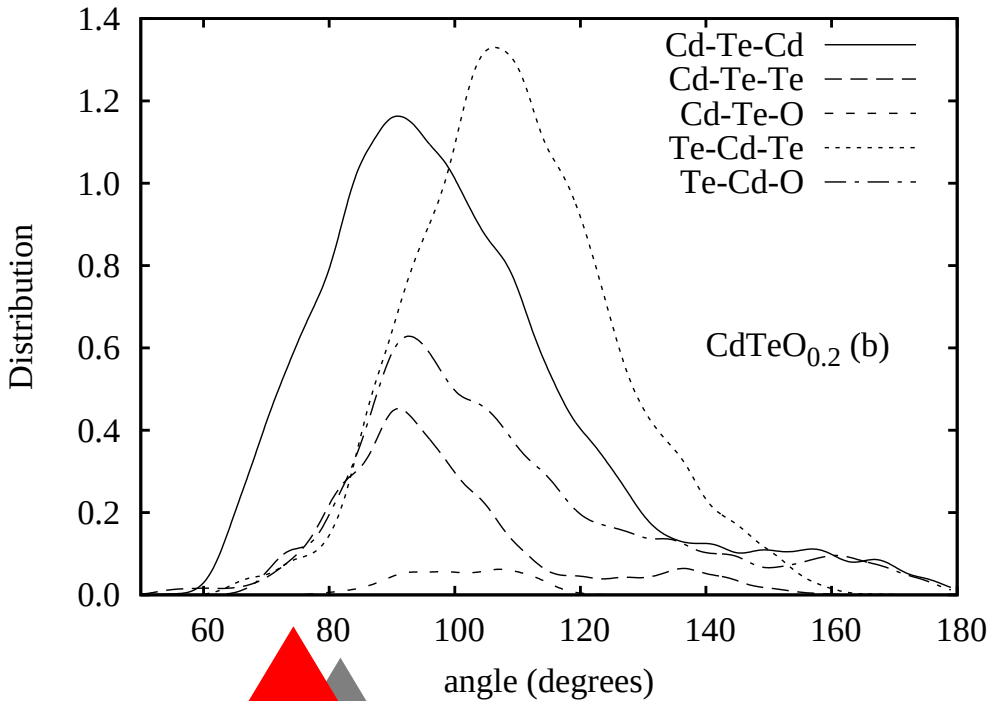




Histogram of coordination number distribution..

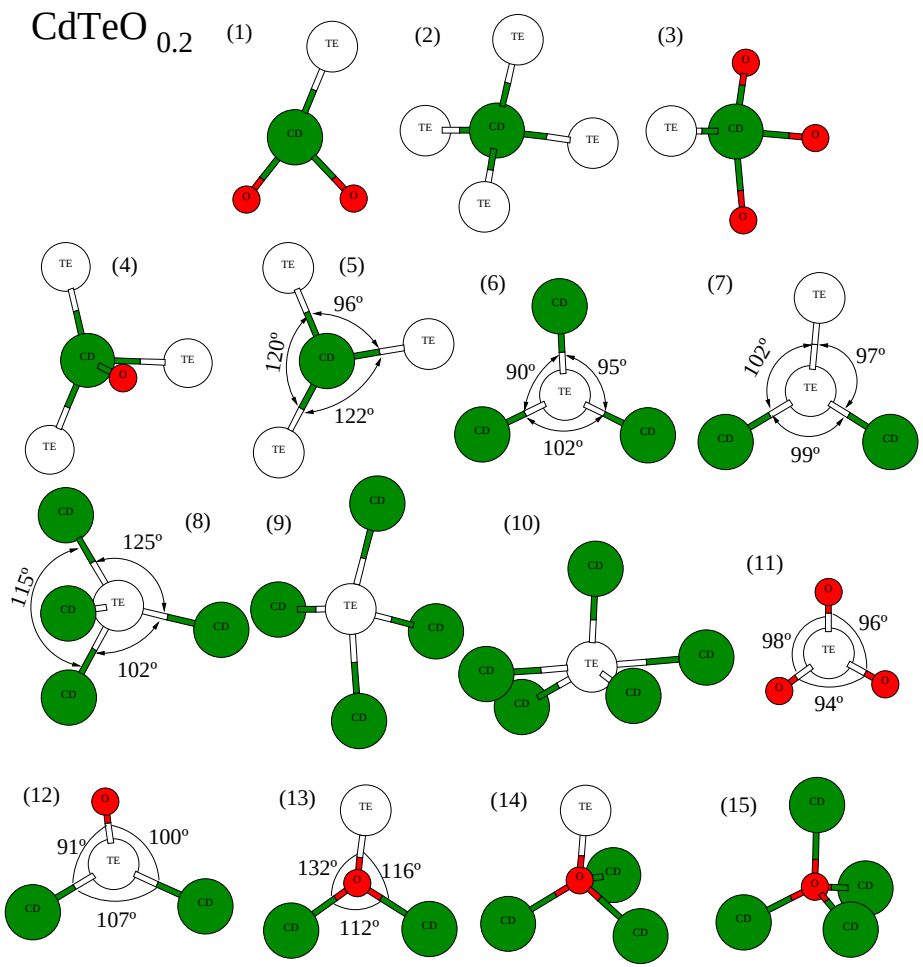
Analysis ($CdTeO_{0.2}$) (III)





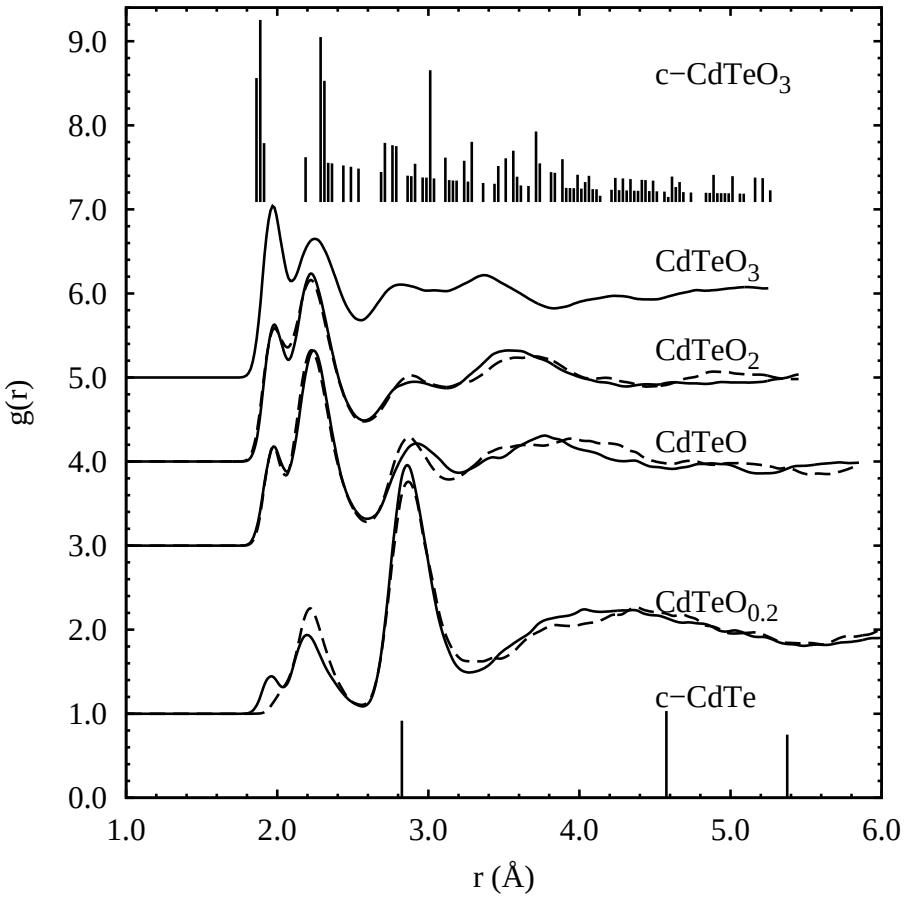
Angle distribution function.

Analysis ($CdTeO_{0.2}$) (IV)



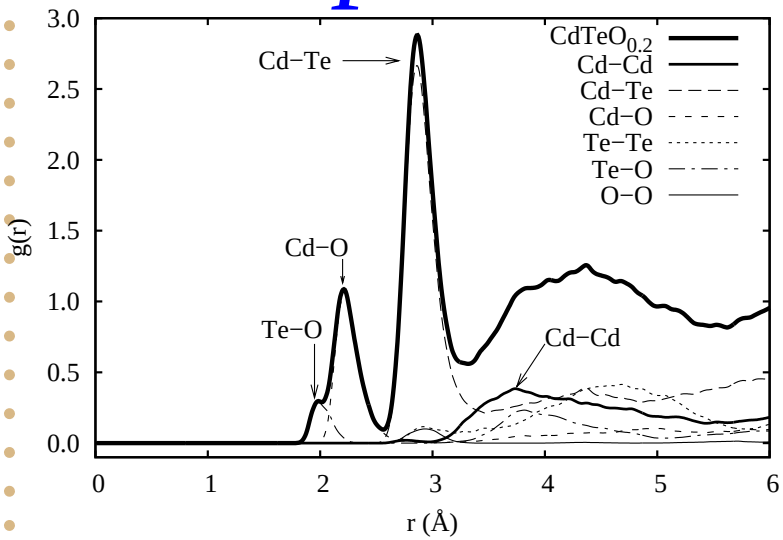
Atomic environments.

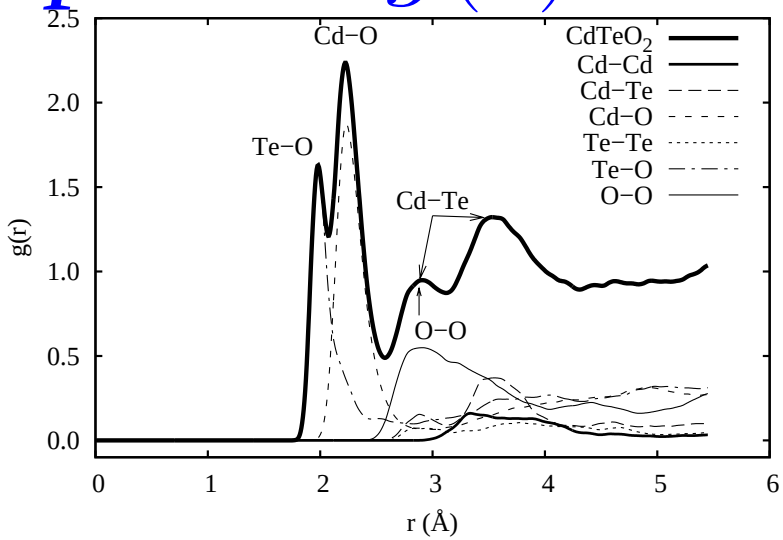
Comparative analysis: $g(r)$

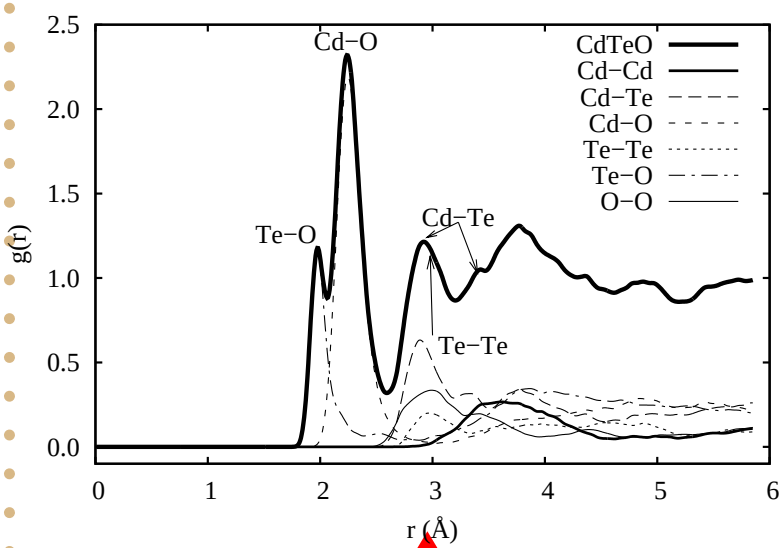


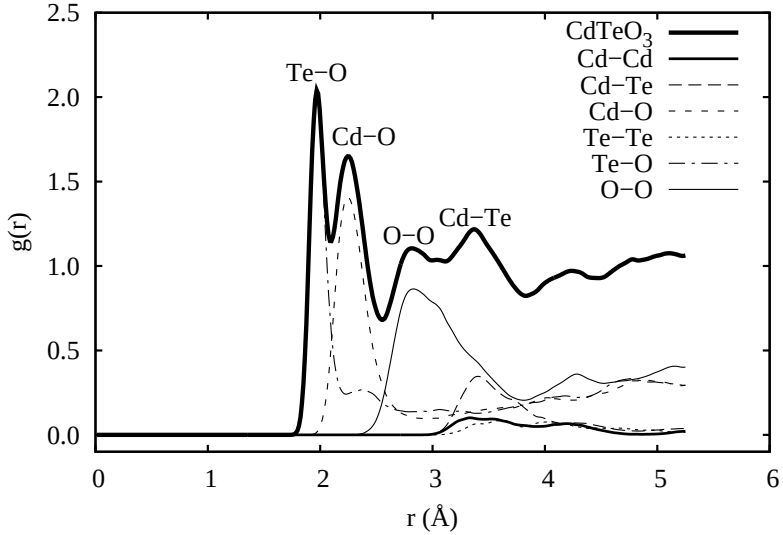
Pair distribution functions of amorphous $CdTeO_{0.2}$, CdTeO, $CdTeO_2$, and $CdTeO_3$, and crystalline c-CdTe and c-$CdTeO_3$.

Comparison of partial $g(r)$







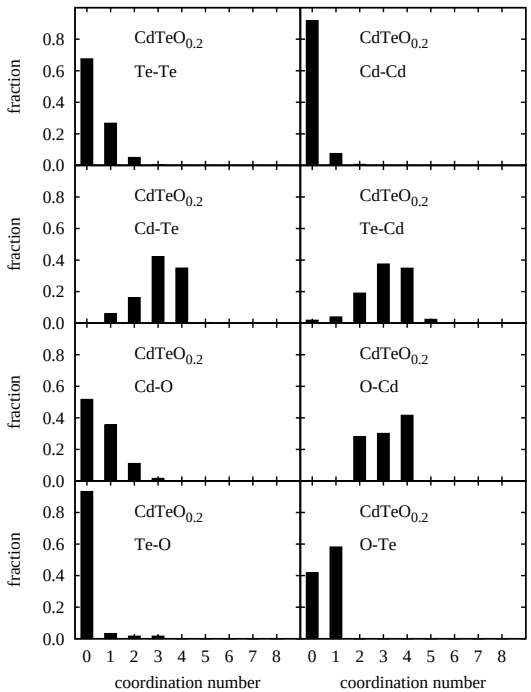


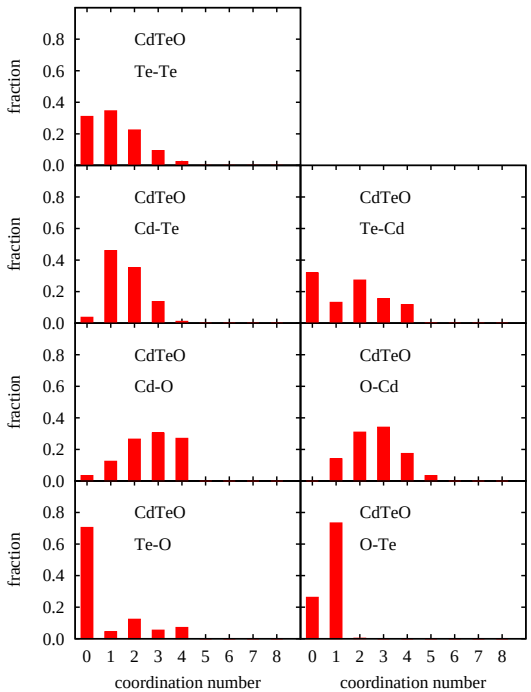
Coordination numbers

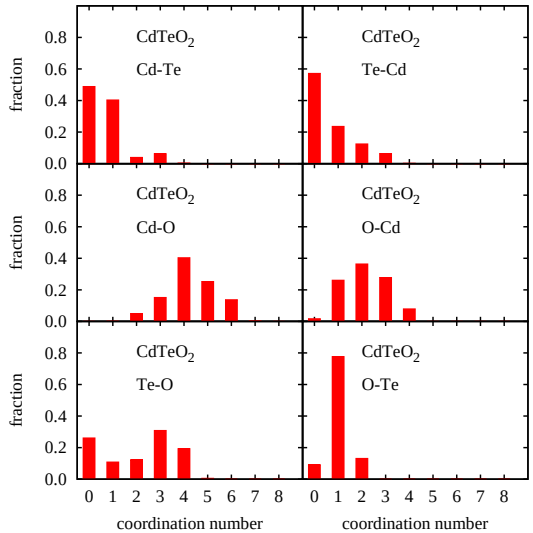
Table 1: . n_{i-j} is the average number of atoms of element j around one atom of element i within a sphere of radius R_{i-j}.

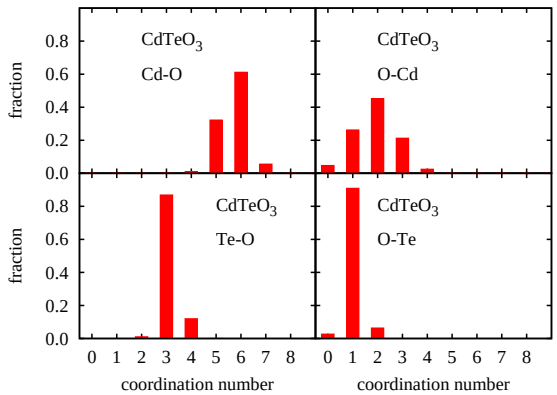
$i-j$	R_{i-j}	n_{i-j}			
		$CdTeO_{0.2}$	CdTeO	$CdTeO_2$	$CdTeO_3$
Te-O	2.32	0.1	0.7	2.1	3.4
O-Te	2.32	0.7	0.7	1.0	1.1
Cd-O	2.90	0.6	2.7	4.3	5.7
O-Cd	2.90	2.8	2.7	2.1	1.9
Cd-Te	3.19	3.1	1.6	0.7	0.2
Te-Cd	3.19	3.1	1.6	0.7	0.2
Te-Te	3.27	0.3	1.2	0.9	0.1

Coordination Numbers Histograms







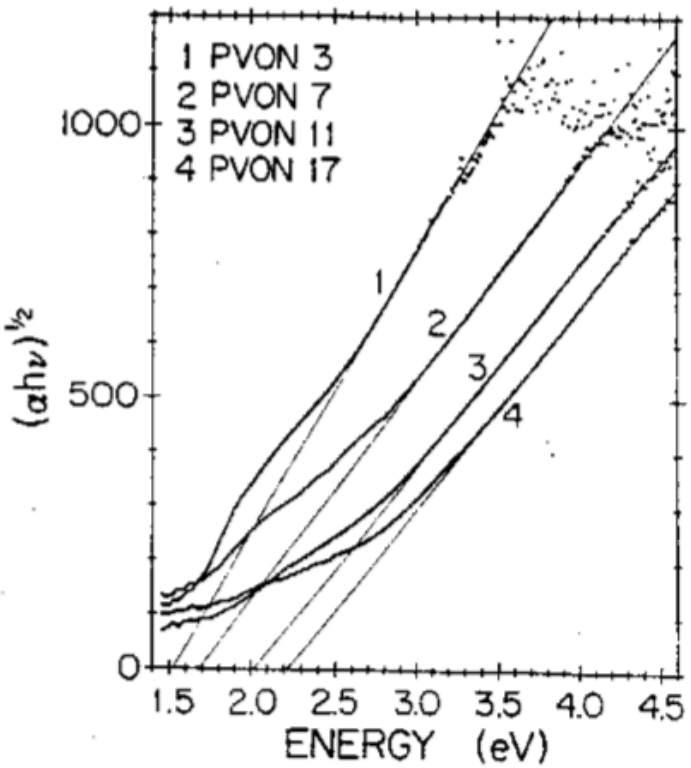


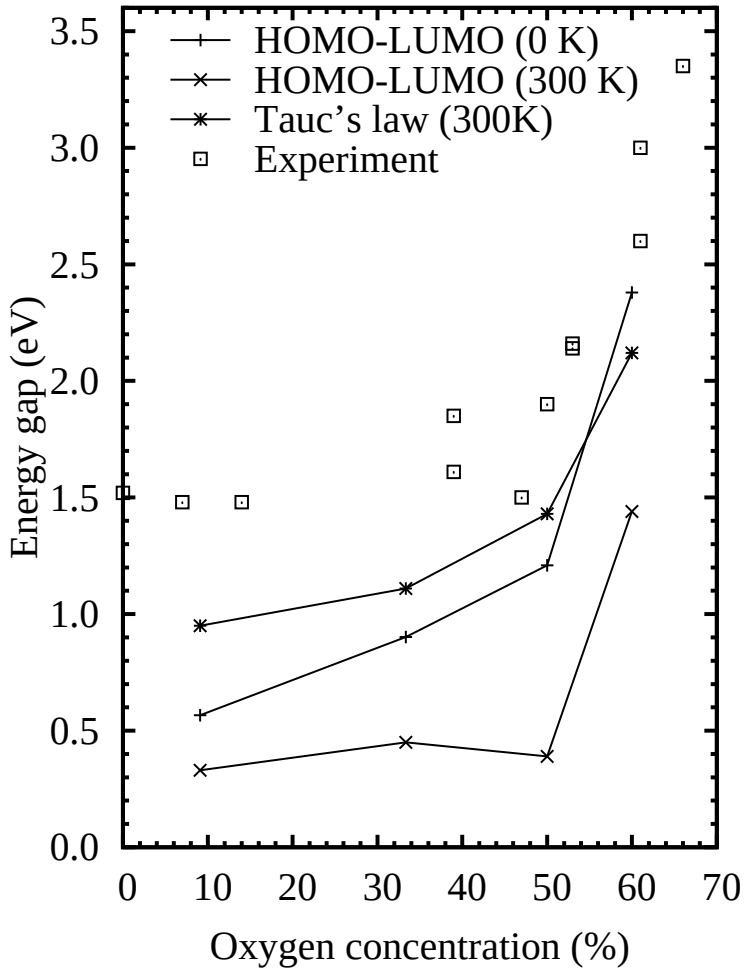
Let us see, for example, the Cd-Te series.

Is the real material?

We need to calculate properties that can be measured experimentally, such as optical spectra, and XPS spectra.

Optical gaps





Optical gap vs oxygen content.

Espinoza *et al*, J. Vac. Sci. Technol. A **11**, 3062 (1993);

E. Menendez-Proupin *et al*, Phys. Rev. B **79**, 014205 (2009).

Reported in

PHYSICAL REVIEW B **79**, 014205 (2009)

Ab initio **molecular dynamics study of amorphous $CdTeO_x$ alloys: Structural properties**

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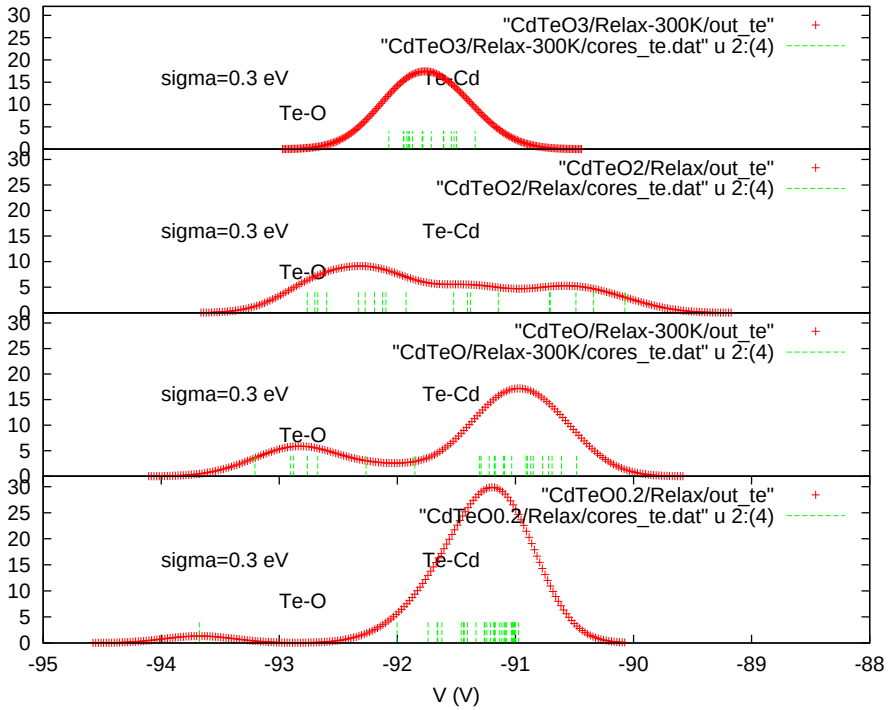
XPS

$$E_{CLS} = \Delta V + \Delta E_R$$

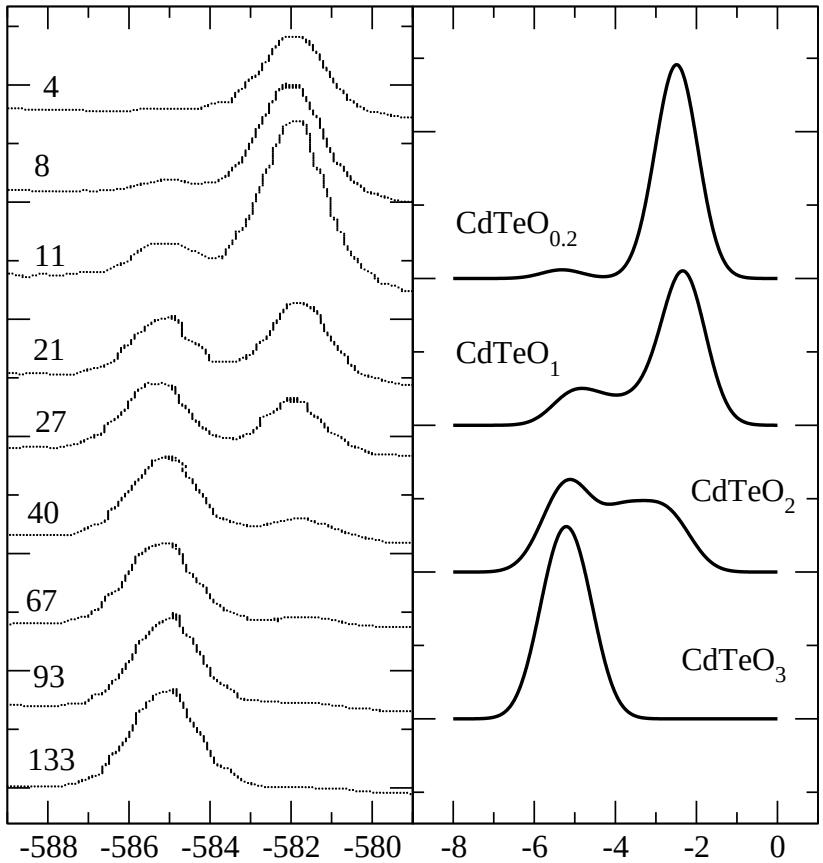
V is the local potential on the excited atom

E_R is the energy of relaxation in the final state



Amezaga, Holström, Menendez-Proupin and Lizarraga.

XPS



Amezaga, Holström, Menendez-Proupin and Lizarraga.

Conclusions

- We obtained structural models.
- Trends with oxygen content.
- Optical gap in qualitative agreement with experiments.
- XPS spectra are in semiquantitative agreement with experiments..
- Prediction of $g_{ij}(r)$ and other indicators that can be measured.

Thank you