Density Functional Theory study of Cd impurities in Molybdenum Trioxide

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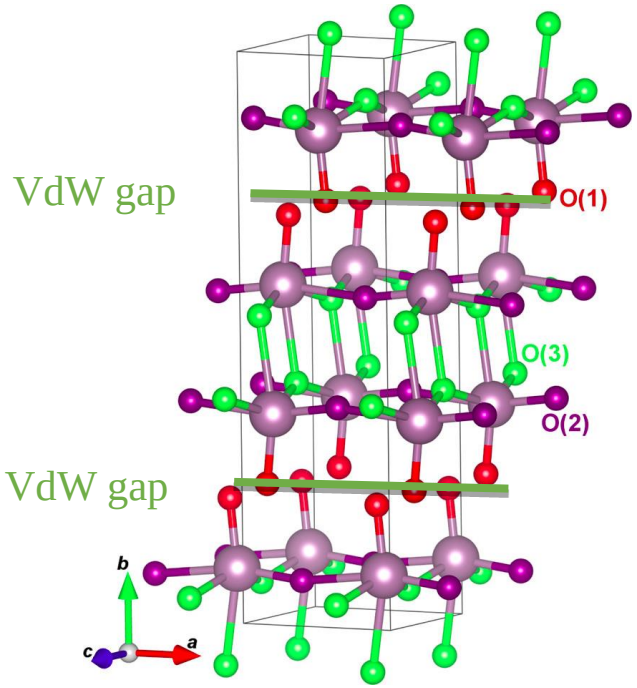
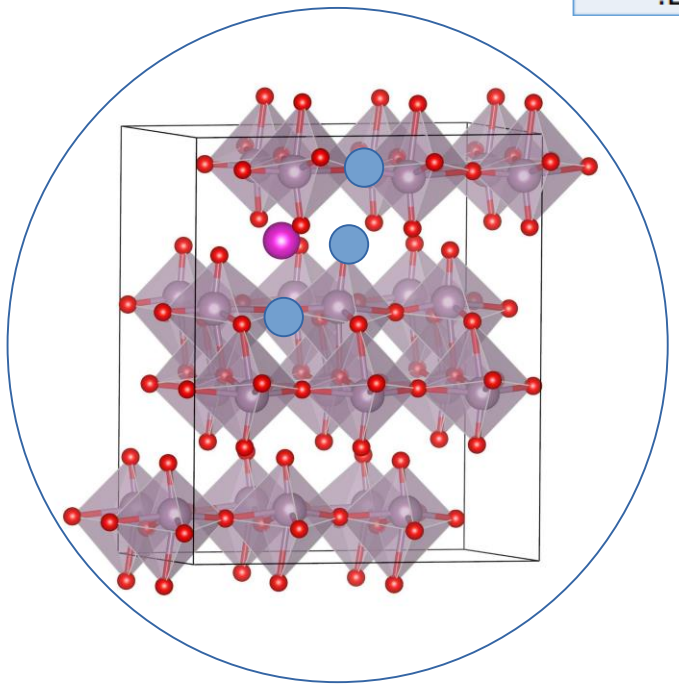
Introduction

- The molybdenum trioxide (MoO_3) is known for its photo-, thermo- and electro-chromism, high catalytic activity.
- the α-MoO_3 is the most stable crystal phase and it has a layered structure consisting of van der Waals bonded sheets of distorted edge-sharing Mo−O_6 octahedra in which Mo atoms are bounded by three distinct types of oxygen atoms.

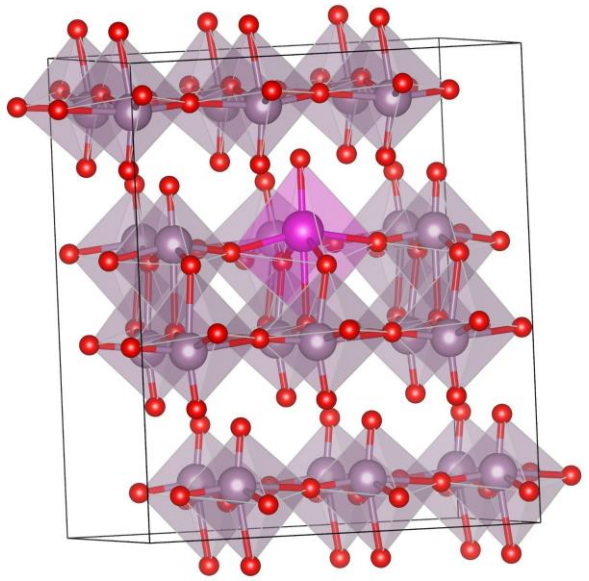


The hyperfine parameters of ^{111m}Cd(^{111}Cd) impurities in α-MoO_3 are investigated by first-principle calculations in the framework of density functional theory (DFT). The Generalized gradient approximation (GGA) plus Hubbard-U corrections for onsite Coulomb interactions are used in the DFT calculations. Also in the calculations, the effect of van der Waals forces between layers are considered.

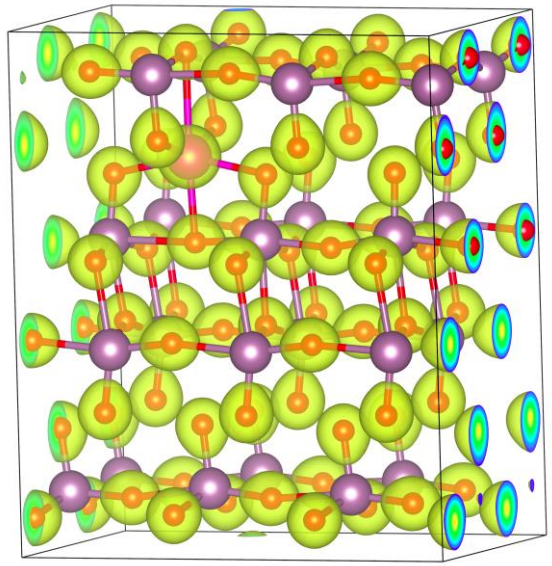
Approximation	a(Å)	%	b(Å)	%	c(Å)	%
GGA-PBE	3.9495	0.34%-	13.8086	0.33%-	3.684	0.34%-
LDA	4.002	0.99%	13.9921	0.99%	3.733	0.99%
PBE-Vdw	3.976	0.15%	13.901	0.33%	3.708	0.05%
.Exp	3.97		13.85		3.71	

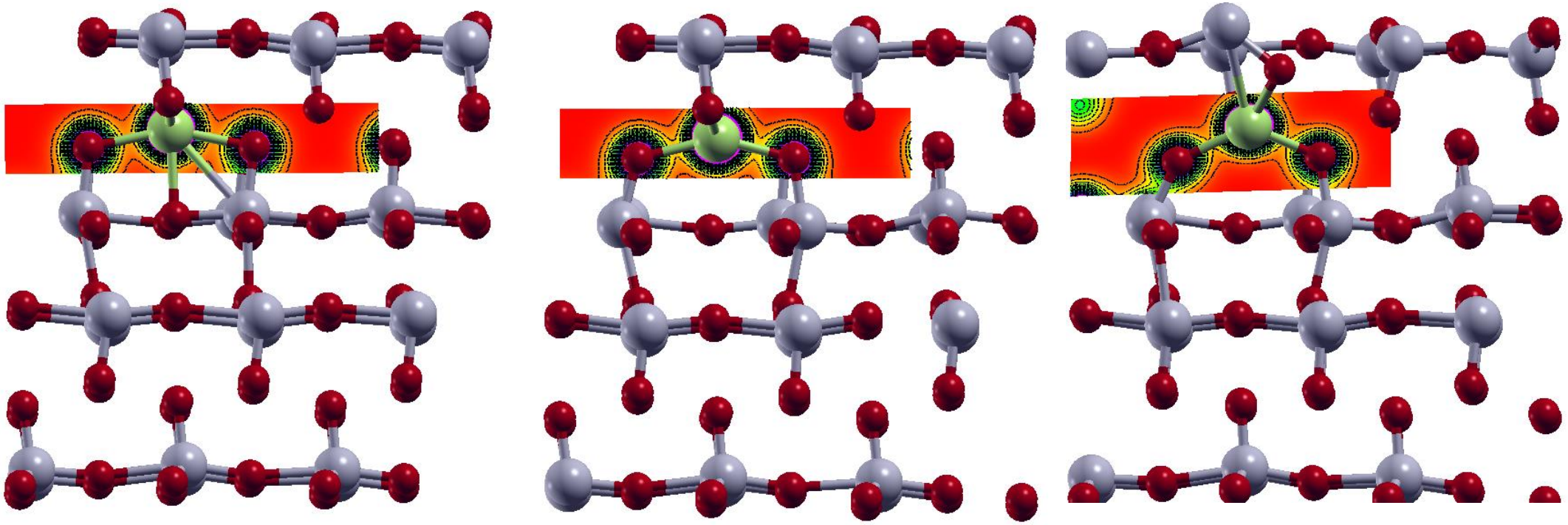


	PBE + SP + U = 6eV (Mo)		
State	Vzz (V/Å^2)	η	E_F (eV)
Cd_I	54.13	0.240	1.3203
Cd_S	45.18	0.957	7.8493



Hyperfine parameters			Electron configuration /Charge state
Configuration	Vzz ($V/Å^2$)	η	d
3x1x2 / GGA+U	54.13	0.240	$[Kr]4(s^2p^6)4d^8/Cd^{4+}$
3x1x2 / GGA+U + 1e	54.98	0.177	$[Kr]4(s^2p^6)4d^8/Cd^{3+}$





Approximation: GGA/PBE with VdW D3 functional			Experimental				
	PBE + U = 6eV (Mo)						
Configuration	Vzz (V/Å^2)	η	EFG	|Vzz| (V/Å^2)	η	%	ºC
Cd_I	54.98	0.177	EFG2	68(1)	0.19(3)	24(3)	24
Cd_I^{VO1}	134.26	0.086	-	-	-	-	-
$^{VO1}Cd_I^{VO1}$	185.17	0.215	-	-	-	-	-
Cd_I^{VO2}	190.24	0.373	EFG 3	195(2)	0.32(1)	13(2)	24
$^{VO2}Cd_I^{VO2}$	48.87	0.255	-	-	-	-	-
$_{VO2}Cd_I^{VO2}$	172.51	0.547	EFG 4	163(1)	0.484(4)	37(3)	150

Conclusion

- After implantation, Cd ion is located at interstitial position in MoO_3 and we find that a vacancy is most likely to form on a 2-fold coordinated O(2) atom.
- the conversion of a former single polaron at Cd_I into a bi-polaron state is happened by increasing the annealing temperature