

Supplementary Information

Demystifying the Dual-functional Electrocatalytic Activity of the 2D Co-Doped NbSSe Janus Transition Metal Dichalcogenide for O₂ Reduction and H₂ Evolution Reactions

Lokesh Yadav¹, Vikash Kumar¹, Kahkasha Parveen¹ and
Srimanta Pakhira^{1,2*}

¹ *Theoretical Condensed Matter Physics and Advanced Computational Materials Science Laboratory, Department of Physics, Indian Institute of Technology Indore (IIT Indore), Simrol, Khandwa Road, Indore, Madhya Pradesh, 453552, India.*

² *Theoretical Condensed Matter Physics and Advanced Computational Materials Science Laboratory, Centre for Advanced Electronics (CAE), Indian Institute of Technology Indore, Simrol, Khandwa Road, Indore, Madhya Pradesh, 453552, India.*

*Corresponding author: spakhira@iiti.ac.in (or) spakhirafsu@gmail.com

The d-band center (ε_d) is used as an electronic descriptor that characterizes the average energy position of the metal d states relative to the Fermi level. It was calculated from the d-projected density of states (PDOS) using this formula:

$$\varepsilon_d = \frac{\int_{E_{min}}^{E_{max}} ED_d(E) dE}{\int_{E_{min}}^{E_{max}} D_d(E) dE}$$

where $D_d(E)$ represents the density of states projected onto the metal d orbitals at energy E. In this expression, the numerator corresponds to the energy-weighted distribution of the d states, while the denominator represents the total contribution of the d states within the selected energy range. All energies were referenced to the Fermi level, so the calculated ε_d directly reflects the average position of the metal d states relative to the Fermi level. The integration was performed

over an energy range from -10 to 1.5 eV relative to the Fermi level, which sufficiently captures the relevant occupied and d-state contributions of the metal atom near the Fermi level. All the calculated values of ε_d for the Co atom in the Co_NbSSe Janus TMD material and for all key ORR intermediates are summarized in Table 1.

Table 1. The computed values of d-band center (ε_d) for the Co atom in the Co_NbSSe Janus TMD material and for all key ORR intermediates.

System	ε_d (eV)
Co NbSSe	0.57
O ₂ * Co NbSSe	0.65
2O* Co NbSSe	0.54
OH* O* Co NbSSe	0.91
O* Co NbSSe	0.62
OH* Co NbSSe	0.79
OOH* Co NbSSe	0.74

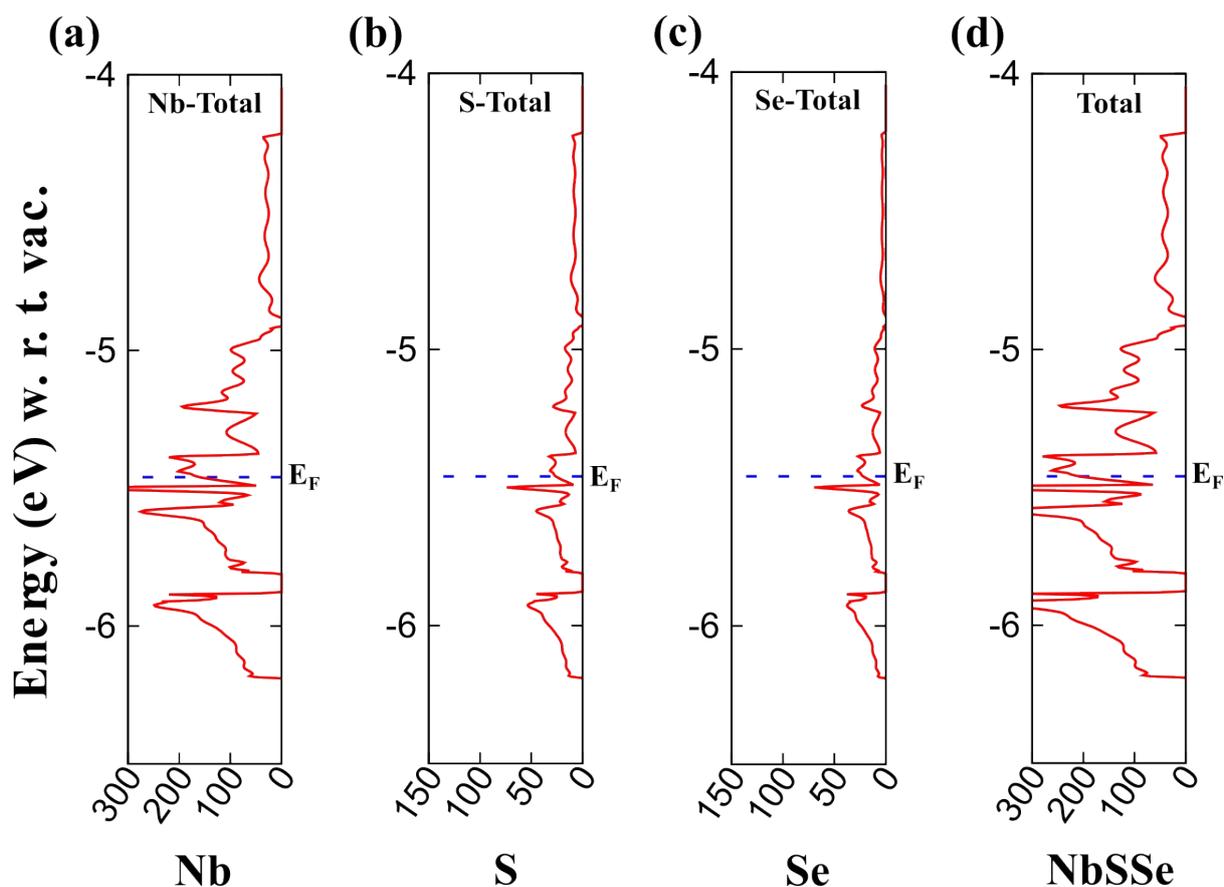


Fig. S1 Projected density of states (PDOS) for the atoms: (a) Nb, (b) S, (c) Se, and (d) total density of states (TDOS) of NbSSe Janus TMD material.

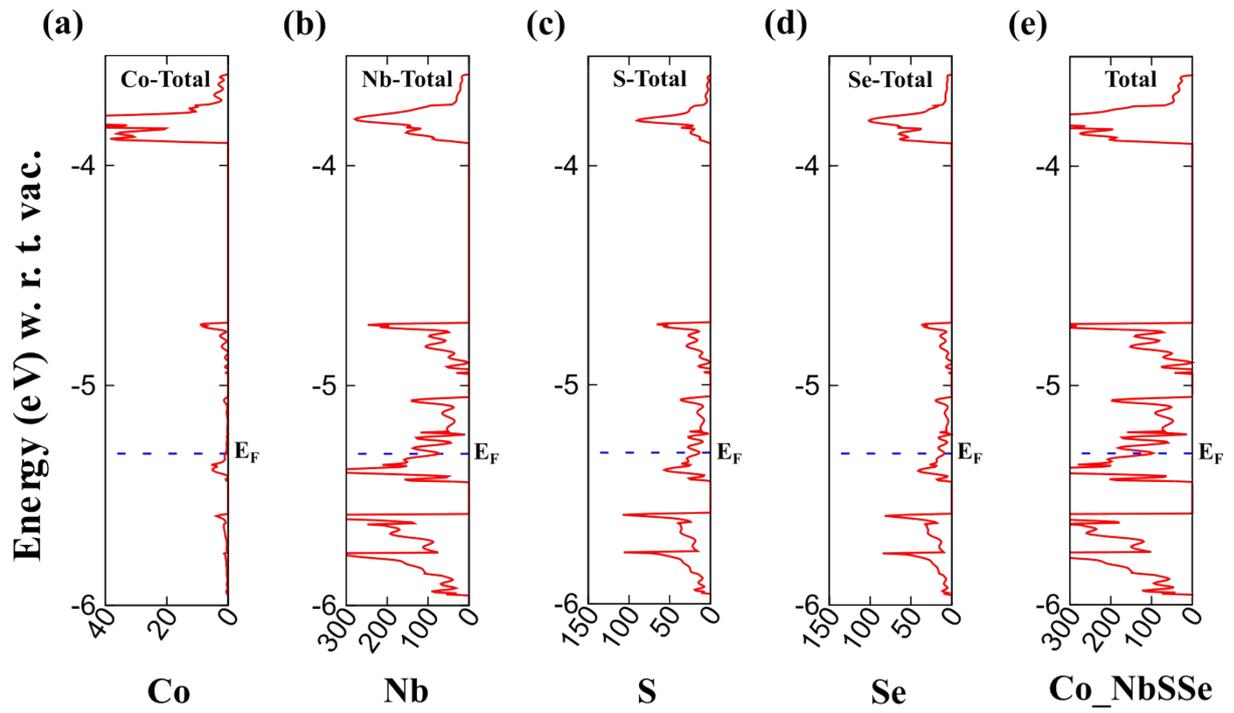


Fig. S2 Projected density of states (PDOS) for the atoms: (a) Co, (b) Nb, (c) S, (d) Se, and (e) total density of states (TDOS) of Co₂NbSSe Janus TMD material.

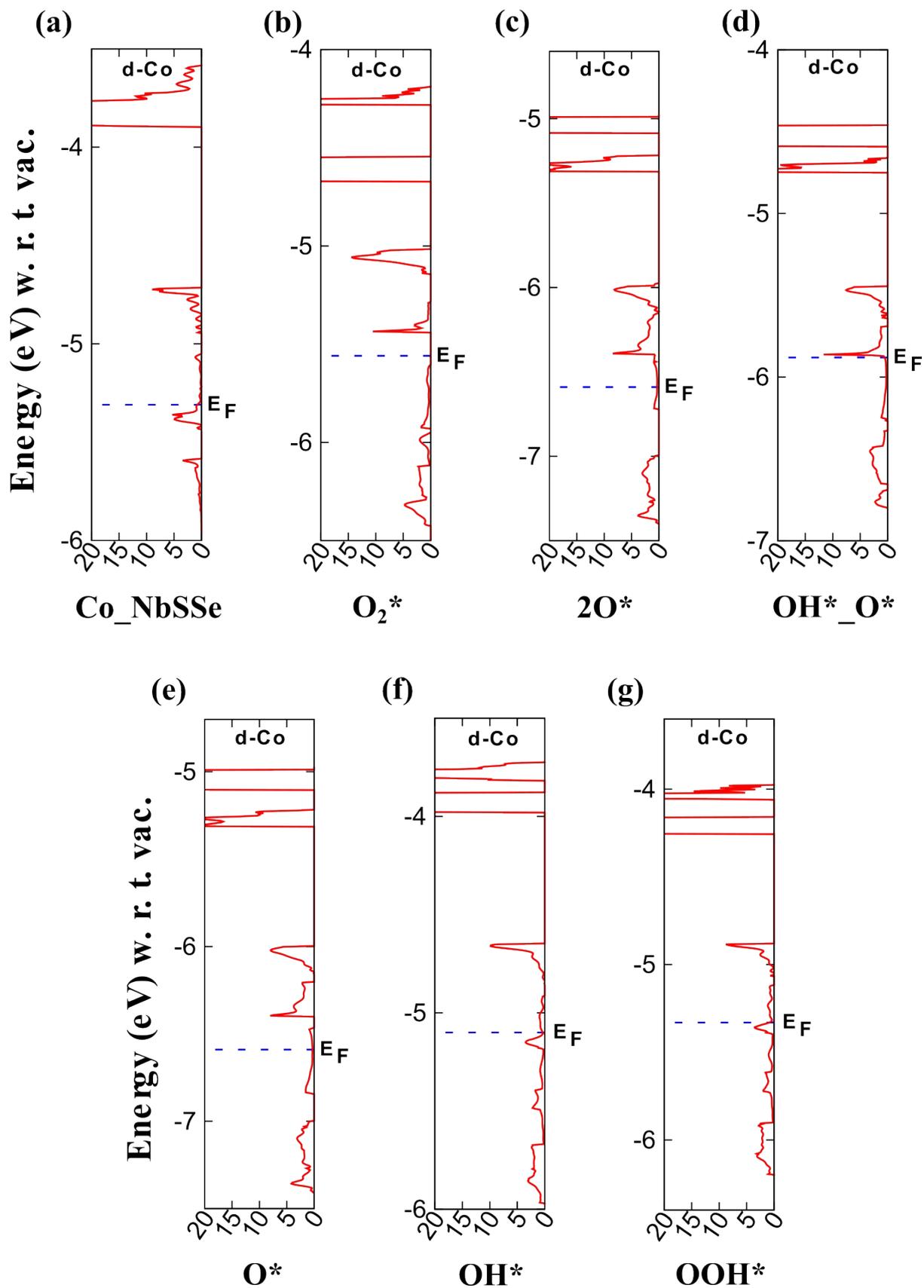


Fig. S3 Projected density of states (PDOS) of the 3d orbitals of the Co atom for the Co₂NbSSe Janus TMD material and the adsorbed ORR intermediates: (a) Co₂NbSSe, (b) O₂*, (c) 2O, (d) OH*₁O*₂, (e) O*, (f) OH*, and (g) OOH*.

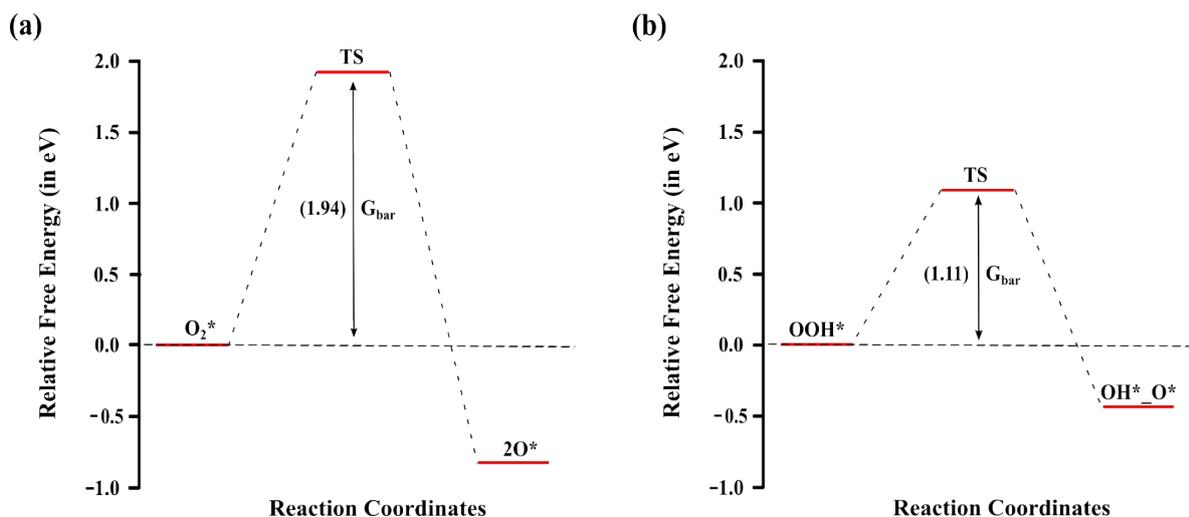


Fig. S4 Energy barriers for (a) O-O bond breaking step in the dissociative pathway and (b) OOH* dissociation step in the associative pathway.

S1: Optimized Structure of pristine 2D monolayer NbSSe (.cif format)

data_NbSSe.out

```

_cell_length_a      10.081491
_cell_length_b      10.081381
_cell_length_c      20.000000
_cell_angle_alpha   90.000000
_cell_angle_beta    90.000000
_cell_angle_gamma   119.999218
_symmetry_space_group_name_H-M  'P 1'
_symmetry_Int_Tables_number      1

```

loop_

_symmetry_equiv_pos_as_xyz

'x, y, z'

loop_

_atom_site_label

_atom_site_type_symbol

_atom_site_fract_x
_atom_site_fract_y
_atom_site_fract_z
NB001 NB -0.000005 -0.000000 0.101078
SE002 SE 0.111110 0.222222 0.185298
S003 S 0.111114 0.222225 0.025505
NB004 NB 0.333328 -0.000001 0.101077
SE005 SE 0.444444 0.222223 0.185298
S006 S 0.444449 0.222226 0.025506
NB007 NB -0.333335 0.000001 0.101078
SE008 SE -0.222223 0.222223 0.185299
S009 S -0.222219 0.222226 0.025505
NB010 NB -0.000007 0.333329 0.101078
SE011 SE 0.111110 -0.444444 0.185297
S012 S 0.111113 -0.444443 0.025506
NB013 NB 0.333326 0.333329 0.101077
SE014 SE 0.444444 -0.444444 0.185297
S015 S 0.444448 -0.444442 0.025506
NB016 NB -0.333337 0.333331 0.101078
SE017 SE -0.222223 -0.444444 0.185298
S018 S -0.222220 -0.444443 0.025506
NB019 NB -0.000005 -0.333333 0.101077
SE020 SE 0.111110 -0.111111 0.185298
S021 S 0.111114 -0.111108 0.025505
NB022 NB 0.333328 -0.333333 0.101077
SE023 SE 0.444444 -0.111111 0.185297
S024 S 0.444449 -0.111107 0.025506
NB025 NB -0.333335 -0.333331 0.101077
SE026 SE -0.222223 -0.111111 0.185298
S027 S -0.222219 -0.111108 0.025505

S2: Optimized Structure of equilibrium 2D monolayer Co-doped NbSSe (.cif format)

data_Co_NbSSe.out

_cell_length_a 10.011793
_cell_length_b 10.011705
_cell_length_c 20.000000
_cell_angle_alpha 90.000000
_cell_angle_beta 90.000000
_cell_angle_gamma 119.999738
_symmetry_space_group_name_H-M 'P 1'
_symmetry_Int_Tables_number 1

loop_

_symmetry_equiv_pos_as_xyz

'x, y, z'

loop_

_atom_site_label

_atom_site_type_symbol

_atom_site_fract_x

_atom_site_fract_y

_atom_site_fract_z

NB001 NB -0.000006 -0.000002 0.100072

SE002 SE 0.111137 0.222273 0.185202

S003 S 0.111676 0.223344 0.023949

NB004 NB 0.331715 -0.000026 0.100332

SE005 SE 0.444681 0.222342 0.185425

S006 S 0.445446 0.222724 0.024389

NB007 NB -0.331745 -0.000024 0.100330

SE008 SE -0.222344 0.222339 0.185424

S009 S -0.222719 0.222728 0.024389

NB010 NB 0.000021 0.331733 0.100333

SE011 SE 0.118096 -0.440951 0.181736

S012 S 0.121583 -0.439208 0.028780

NB013 NB 0.331714 0.331742 0.100332
 SE014 SE 0.440954 -0.440948 0.181736
 S015 S 0.439206 -0.439208 0.028770
 NB016 NB -0.333344 0.333329 0.100820
 SE017 SE -0.222344 -0.444681 0.185423
 S018 S -0.222719 -0.445445 0.024389
 NB019 NB 0.000021 -0.331709 0.100333
 SE020 SE 0.111137 -0.111133 0.185202
 S021 S 0.111676 -0.111666 0.023949
 CO022 CO 0.333333 -0.333332 0.101953
 SE023 SE 0.440954 -0.118096 0.181737
 S024 S 0.439206 -0.121584 0.028770
 NB025 NB -0.331744 -0.331717 0.100330
 SE026 SE -0.222275 -0.111136 0.185199
 S027 S -0.223337 -0.111667 0.023947

S3: Optimized Structure of various equilibrium reaction intermediates during the ORR process (.cif format)

(a) O₂*_Co_NbSSe

data_O2_Co_NbSSe.out

```

_cell_length_a          10.063296
_cell_length_b          10.060928
_cell_length_c          20.000000
_cell_angle_alpha       90.000000
_cell_angle_beta        90.000000
_cell_angle_gamma       120.035808
_symmetry_space_group_name_H-M  'P 1'
_symmetry_Int_Tables_number  1

loop_
_symmetry_equiv_pos_as_xyz
  'x, y, z'

```

loop_

_atom_site_label

_atom_site_type_symbol

_atom_site_fract_x

_atom_site_fract_y

_atom_site_fract_z

NB001 NB 0.002688 -0.002268 0.099956

SE002 SE 0.109849 0.220618 0.184660

S003 S 0.109465 0.221482 0.023171

NB004 NB 0.332090 0.000511 0.101050

SE005 SE 0.445733 0.221477 0.186017

S006 S 0.448459 0.220071 0.023368

NB007 NB -0.332685 0.001201 0.100134

SE008 SE -0.221304 0.221597 0.185767

S009 S -0.221702 0.222147 0.024568

NB010 NB -0.000933 0.332982 0.100202

SE011 SE 0.112885 -0.442193 0.182974

S012 S 0.120069 -0.438953 0.028964

NB013 NB 0.326134 0.315482 0.098639

SE014 SE 0.439842 -0.439825 0.167152

S015 S 0.438777 -0.438170 0.033650

NB016 NB -0.332239 0.332818 0.101379

SE017 SE -0.221046 -0.445243 0.186093

S018 S -0.219586 -0.447766 0.023430

NB019 NB -0.000164 -0.331761 0.101074

SE020 SE 0.111690 -0.111206 0.185986

S021 S 0.113146 -0.112761 0.023914

CO022 CO 0.326001 -0.325602 0.103476

SE023 SE 0.442816 -0.112356 0.182948

S024 S 0.439243 -0.119679 0.028922

NB025 NB -0.315134 -0.325643 0.098790

SE026 SE -0.220548 -0.110310 0.184458

S027 S -0.221070 -0.109076 0.023179

O028 O 0.439177 -0.443323 0.267935

O029 O 0.374188 -0.372159 0.296126

(b) 2O*_Co_NbSSe

data_2O_Co_NbSSe.out

_cell_length_a 10.053751

_cell_length_b 10.049938

_cell_length_c 20.000000

_cell_angle_alpha 90.000000

_cell_angle_beta 90.000000

_cell_angle_gamma 119.987209

_symmetry_space_group_name_H-M 'P 1'

_symmetry_Int_Tables_number 1

loop_

_symmetry_equiv_pos_as_xyz

'x, y, z'

loop_

_atom_site_label

_atom_site_type_symbol

_atom_site_fract_x

_atom_site_fract_y

_atom_site_fract_z

NB001 NB 0.003806 0.000013 0.101694

SE002 SE 0.112995 0.220987 0.186880

S003 S 0.108889 0.219866 0.023381

NB004 NB 0.324222 0.000860 0.099013

SE005 SE 0.445765 0.220975 0.184887

S006 S 0.452675 0.224403 0.024292

NB007 NB -0.319675 0.002970 0.100089
 SE008 SE -0.219337 0.221064 0.186563
 S009 S -0.218938 0.224059 0.025056
 NB010 NB 0.003217 0.333189 0.101625
 SE011 SE 0.119982 -0.441880 0.184000
 S012 S 0.119552 -0.442113 0.028127
 NB013 NB 0.324248 0.319557 0.099004
 SE014 SE 0.443945 -0.445484 0.175729
 S015 S 0.441318 -0.440300 0.032962
 NB016 NB -0.328413 0.333912 0.102094
 SE017 SE -0.219331 -0.444178 0.186560
 S018 S -0.218928 -0.446775 0.025042
 NB019 NB 0.003202 -0.333753 0.101619
 SE020 SE 0.112975 -0.111782 0.186884
 S021 S 0.108884 -0.114756 0.023379
 CO022 CO 0.324306 -0.339753 0.101173
 SE023 SE 0.443886 -0.114438 0.175749
 S024 S 0.441317 -0.122172 0.032972
 NB025 NB -0.319647 -0.326412 0.100067
 SE026 SE -0.219278 -0.111543 0.186773
 S027 S -0.217547 -0.110640 0.023459
 O028 O 0.433453 -0.444247 0.258116
 O029 O 0.433406 -0.125918 0.258145

(c) OH*_O*_Co_NbSSe

data_OH_O_Co_NbSSe.out

_cell_length_a	10.067862
_cell_length_b	10.054666
_cell_length_c	20.000000
_cell_angle_alpha	90.000000
_cell_angle_beta	90.000000
_cell_angle_gamma	119.928188

_symmetry_space_group_name_H-M 'P 1'
_symmetry_Int_Tables_number 1

loop_

_symmetry_equiv_pos_as_xyz
'x, y, z'

loop_

_atom_site_label
_atom_site_type_symbol
_atom_site_fract_x
_atom_site_fract_y
_atom_site_fract_z
NB001 NB 0.007040 0.003266 0.102797
SE002 SE 0.113858 0.222975 0.188440
S003 S 0.113814 0.223441 0.025170
NB004 NB 0.327692 0.006569 0.101662
SE005 SE 0.449052 0.224248 0.187741
S006 S 0.452990 0.226618 0.025802
NB007 NB -0.313778 0.009640 0.100536
SE008 SE -0.217407 0.223617 0.187791
S009 S -0.215949 0.227735 0.025332
NB010 NB 0.003417 0.333973 0.102562
SE011 SE 0.116875 -0.442970 0.184500
S012 S 0.120607 -0.440809 0.029076
NB013 NB 0.327722 0.321773 0.101941
SE014 SE 0.446428 -0.438575 0.174819
S015 S 0.443150 -0.439729 0.033958
NB016 NB -0.327979 0.334961 0.103274
SE017 SE -0.217483 -0.442216 0.187391
S018 S -0.216465 -0.445336 0.025495
NB019 NB 0.003843 -0.332348 0.102258

SE020 SE 0.113791 -0.110803 0.188087
S021 S 0.113850 -0.110510 0.025036
CO022 CO 0.323577 -0.340263 0.103169
SE023 SE 0.444020 -0.120982 0.171889
S024 S 0.443387 -0.118210 0.034179
NB025 NB -0.316085 -0.325385 0.100341
SE026 SE -0.216737 -0.109404 0.186710
S027 S -0.214394 -0.107677 0.024206
O028 O 0.437653 -0.408349 0.257335
O029 O 0.432193 -0.151651 0.259257
H030 H 0.438698 -0.250089 0.265924

(d) O*_Co_NbSSe

data_O_Co_NbSSe.out

_cell_length_a 10.026623
_cell_length_b 10.026641
_cell_length_c 20.000000
_cell_angle_alpha 90.000000
_cell_angle_beta 90.000000
_cell_angle_gamma 119.962278
_symmetry_space_group_name_H-M 'P 1'
_symmetry_Int_Tables_number 1

loop_

_symmetry_equiv_pos_as_xyz
'x, y, z'

loop_

_atom_site_label
_atom_site_type_symbol
_atom_site_fract_x
_atom_site_fract_y

_atom_site_fract_z

NB001 NB 0.002146 -0.002031 0.101109
SE002 SE 0.111251 0.220831 0.186231
S003 S 0.108668 0.220052 0.023640
NB004 NB 0.331676 -0.001926 0.101008
SE005 SE 0.445344 0.221014 0.185610
S006 S 0.448739 0.221043 0.024496
NB007 NB -0.332770 -0.001395 0.100973
SE008 SE -0.220834 0.220959 0.186286
S009 S -0.220831 0.220970 0.025096
NB010 NB 0.001518 0.332870 0.100976
SE011 SE 0.118813 -0.441406 0.182496
S012 S 0.120690 -0.440298 0.028473
NB013 NB 0.325062 0.319732 0.099357
SE014 SE 0.443405 -0.443277 0.174667
S015 S 0.439887 -0.439786 0.032998
NB016 NB -0.331089 0.331157 0.101524
SE017 SE -0.220901 -0.445228 0.185589
S018 S -0.220929 -0.448641 0.024505
NB019 NB 0.002060 -0.331515 0.101000
SE020 SE 0.112549 -0.112417 0.186430
S021 S 0.112716 -0.112565 0.024154
CO022 CO 0.329733 -0.329601 0.101434
SE023 SE 0.441529 -0.118684 0.182499
S024 S 0.440423 -0.120566 0.028464
NB025 NB -0.319613 -0.324920 0.099346
SE026 SE -0.220713 -0.111132 0.186227
S027 S -0.219917 -0.108521 0.023633
O028 O 0.433476 -0.433350 0.257072

(e) OH*_Co_NbSSe

data_BG_OH_Co_NbSSe.out

_cell_length_a 10.046793
_cell_length_b 10.050000
_cell_length_c 20.000000
_cell_angle_alpha 90.000000
_cell_angle_beta 90.000000
_cell_angle_gamma 120.034510
_symmetry_space_group_name_H-M 'P 1'
_symmetry_Int_Tables_number 1

loop_

_symmetry_equiv_pos_as_xyz
'x, y, z'

loop_

_atom_site_label
_atom_site_type_symbol
_atom_site_fract_x
_atom_site_fract_y
_atom_site_fract_z
NB001 NB 0.002631 -0.000137 0.101324
SE002 SE 0.110737 0.223182 0.185907
S003 S 0.109118 0.222989 0.024367
NB004 NB 0.332552 0.003406 0.102252
SE005 SE 0.445096 0.223673 0.187170
S006 S 0.447325 0.221993 0.024414
NB007 NB -0.333461 0.003220 0.101005
SE008 SE -0.221466 0.223762 0.186626
S009 S -0.221622 0.224196 0.025337
NB010 NB -0.000453 0.335109 0.101059
SE011 SE 0.115270 -0.439256 0.183366
S012 S 0.120264 -0.436699 0.029729
NB013 NB 0.325999 0.318724 0.100073

SE014 SE 0.442320 -0.438285 0.168801
S015 S 0.438676 -0.437644 0.033402
NB016 NB -0.332891 0.333919 0.102061
SE017 SE -0.221697 -0.442769 0.186517
S018 S -0.219910 -0.446093 0.024179
NB019 NB -0.000512 -0.329471 0.101870
SE020 SE 0.111500 -0.109382 0.187075
S021 S 0.113291 -0.110196 0.025001
CO022 CO 0.327772 -0.325413 0.103637
SE023 SE 0.441170 -0.113378 0.183647
S024 S 0.438807 -0.117891 0.029676
NB025 NB -0.316552 -0.323658 0.099017
SE026 SE -0.221715 -0.109076 0.185679
S027 S -0.220550 -0.105898 0.024174
O028 O 0.437190 -0.435181 0.258917
H029 H -0.482839 -0.332796 0.273146

(f) OOH*_Co_NbSSe

data_OOH_Co_NbSSe.out

_cell_length_a 10.055429
_cell_length_b 10.050915
_cell_length_c 20.000000
_cell_angle_alpha 90.000000
_cell_angle_beta 90.000000
_cell_angle_gamma 119.942661
_symmetry_space_group_name_H-M 'P 1'
_symmetry_Int_Tables_number 1

loop_

_symmetry_equiv_pos_as_xyz

'x, y, z'

loop_

_atom_site_label

_atom_site_type_symbol

_atom_site_fract_x

_atom_site_fract_y

_atom_site_fract_z

NB001 NB -0.005651 -0.004878 0.100282

SE002 SE 0.101295 0.217636 0.185112

S003 S 0.100019 0.218662 0.023565

NB004 NB 0.323083 -0.002274 0.101690

SE005 SE 0.436319 0.218380 0.186554

S006 S 0.439570 0.217243 0.024144

NB007 NB -0.340831 -0.001294 0.100874

SE008 SE -0.229900 0.218901 0.186626

S009 S -0.230539 0.219285 0.025207

NB010 NB -0.009865 0.330443 0.100868

SE011 SE 0.105773 -0.443995 0.183345

S012 S 0.111413 -0.442143 0.029543

NB013 NB 0.316202 0.312569 0.099167

SE014 SE 0.429291 -0.445917 0.168919

S015 S 0.431672 -0.440840 0.034237

NB016 NB -0.340924 0.329688 0.102197

SE017 SE -0.229888 -0.448209 0.187183

S018 S -0.229197 -0.450292 0.024470

NB019 NB -0.009733 -0.335242 0.101756

SE020 SE 0.102930 -0.114252 0.186530

S021 S 0.104447 -0.116238 0.024416

CO022 CO 0.318067 -0.330420 0.103949

SE023 SE 0.433460 -0.117616 0.183272

S024 S 0.430323 -0.123139 0.029791

NB025 NB -0.324224 -0.328080 0.100409

SE026 SE -0.227263 -0.111055 0.185088

S027 S -0.229942 -0.112150 0.023991

O028 O 0.400134 -0.464402 0.260577

O029 O -0.483747 -0.325998 0.294881

H030 H 0.469233 -0.260743 0.292560