

## Electronic Supplementary Information

# Introducing antiferromagnetic ordering on the surface states of **Bi<sub>2</sub>Se<sub>3</sub>** topological insulator by Europium doping

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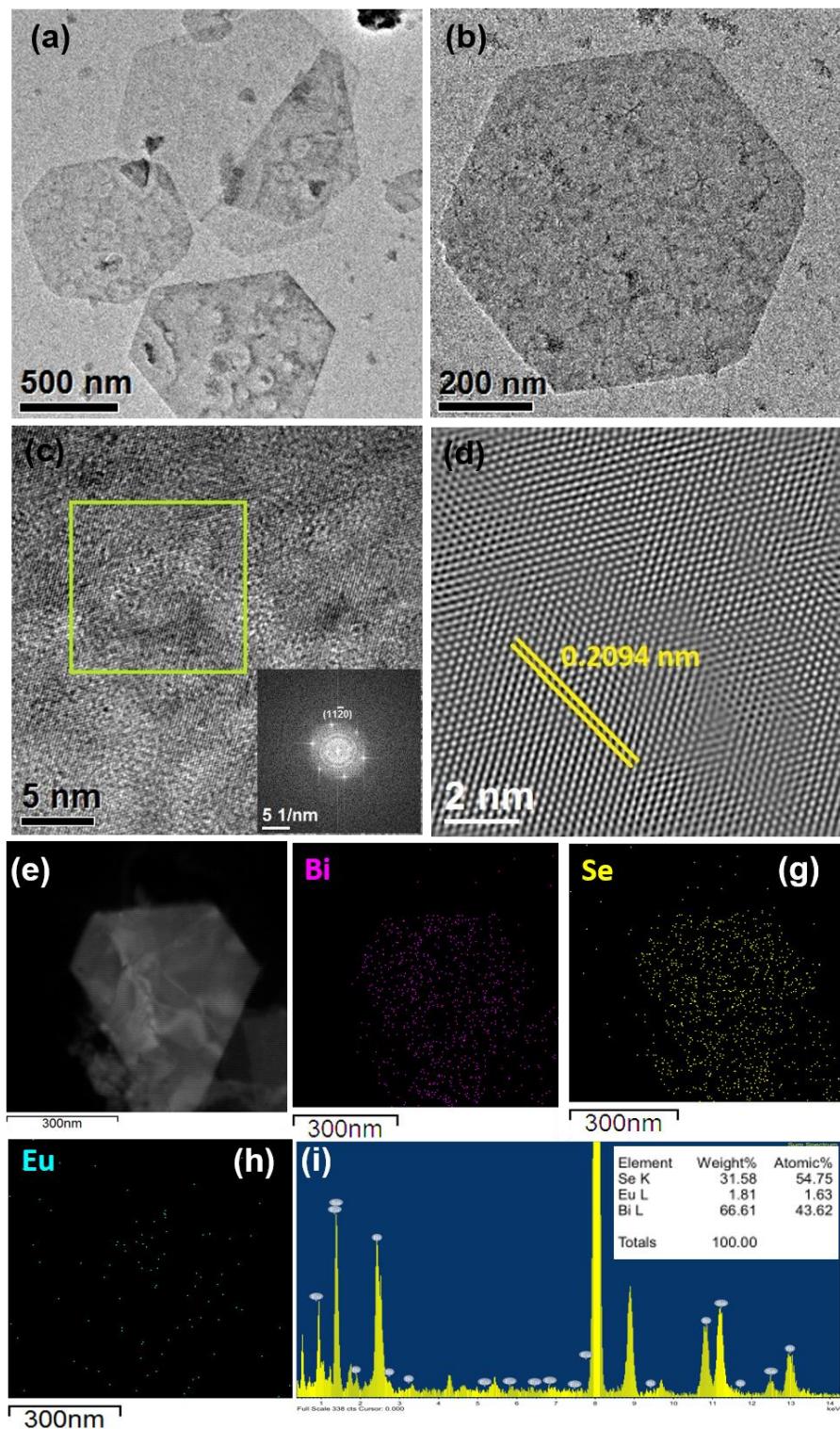
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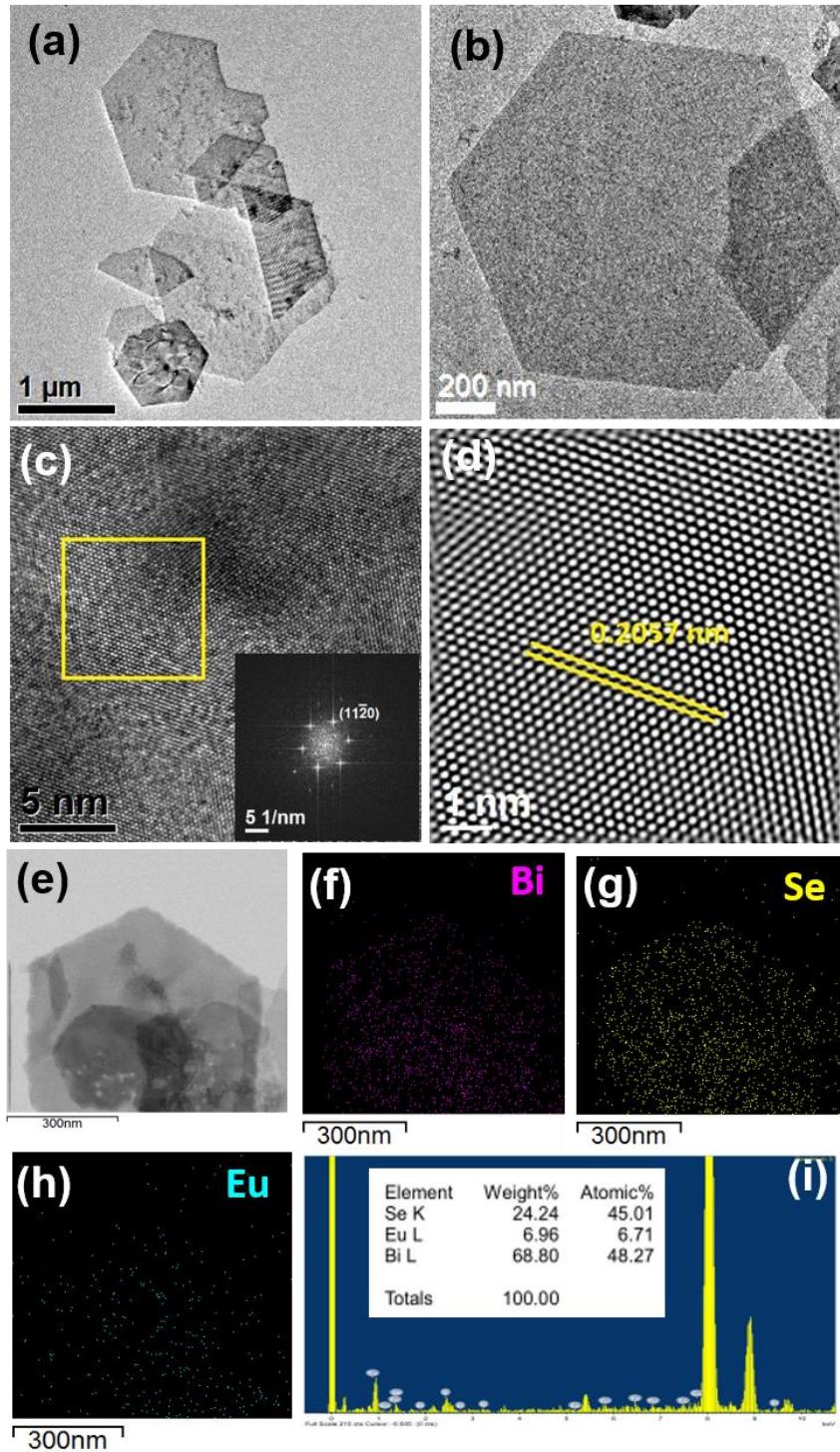
¶ Present Address: CSIR-Central Glass and Ceramic Research Institute, 196 Raja S. C. Mullick Road, Kolkata 700 032, India

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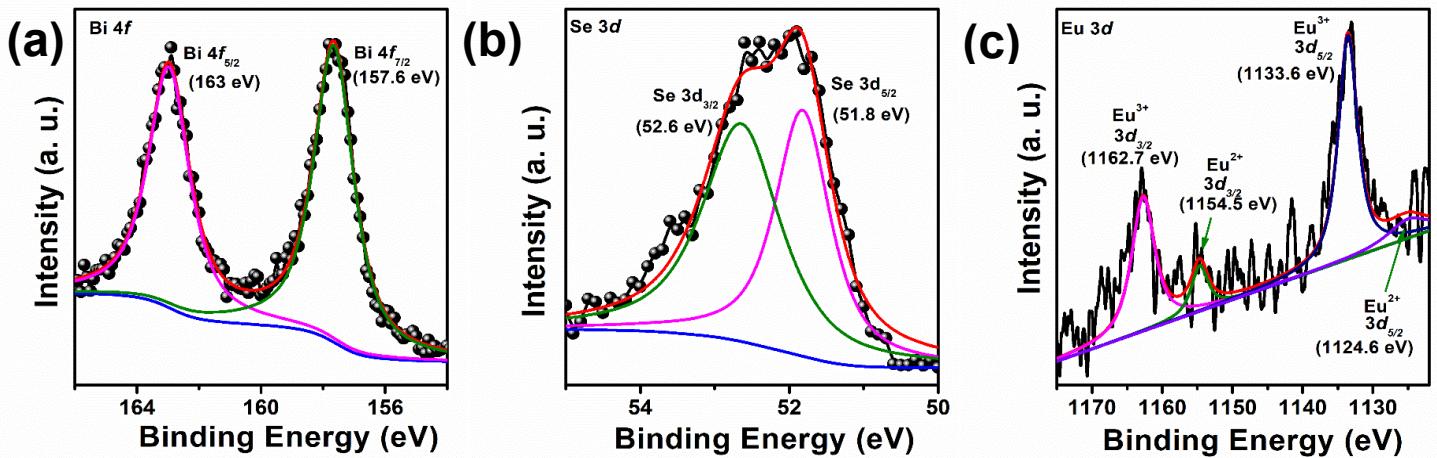
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**Figure S1.** (a) Large area inverted TEM image of undoped 5% Eu doped  $\text{Bi}_2\text{Se}_3$  NSs. (b) A closer view of a single microsheet. (c) HRTEM lattice image of a single MS; the inset shows the FFT pattern of the (11-20) group of planes as obtained from the yellow squared region of HRTEM image of  $\text{Bi}_2\text{Se}_3$ . (d) Reconstructed HRTEM image showing the  $d$  spacing value of 0.209 nm corresponding to the group of planes (11-20). (e) Scanning TEM image of  $\text{Bi}_2\text{Se}_3$  nanosheet and corresponding STEM elemental mapping of (f) Bi, (g) Se and (h) Eu atoms, respectively. (i) Energy dispersive X-ray (EDX) spectrum of  $\text{Bi}_2\text{Se}_3$  MS showing the atomic percentage of different elements.



**Figure S2.** (a) Large area inverted TEM image of undoped 10% Eu doped  $\text{Bi}_2\text{Se}_3$  NSs. (b) A closer view of a single microsheet. (c) HRTEM lattice image of a single MS; the inset shows the FFT pattern of the (11-20) group of planes as obtained from the yellow squared region of HRTEM image of  $\text{Bi}_2\text{Se}_3$ . (d) Reconstructed HRTEM image showing the  $d$  spacing value of 0.205 nm corresponding to the group of planes (11-20). (e) Scanning TEM image of  $\text{Bi}_2\text{Se}_3$  nanosheet and corresponding STEM elemental mapping of (f) Bi, (g) Se and (h) Eu atoms, respectively. (i) Energy dispersive X-ray (EDX) spectrum of  $\text{Bi}_2\text{Se}_3$  MS showing the atomic percentage of different elements.



**Figure S3.** Lorentzian fitted XPS spectrum of the elements:(a) Bi 4f core-level,(b) Se 3d core-level,(c) Eu 3d core-level. The solid lines refer to the fitted peaks with a Shirley baseline, and the symbols correspond to the experimental data.

```
# Bi2Se3
```

```
data_Bi2Se3
```

```
_audit_creation_method
```

```
_cell_length_a 4.1888195996
```

```
_cell_length_b 4.1888195996
```

```
_cell_length_c 30.8113039972
```

```
_cell_angle_alpha 90.0000000000
```

```
_cell_angle_beta 90.0000000000
```

```
_cell_angle_gamma 120.0000000000
```

```
_cell_volume 468.1920387017
```

```
_symmetry_space_group_name_H-M "R -3 2/m (hexagonal axes)"
```

```
_symmetry_Int_Tables_number 166
```

```
_space_group.reference_setting '166:-R 3 2"
```

```
_space_group.transform_Pp_abc a,b,c;0,0,0
```

```
loop_
```

```
_space_group_symop_id
```

```
_space_group_symop_operation_xyz
```

```
1 x,y,z
```

```
2 -y,x-y,z
```

```
3 -x+y,-x,z
```

```
4 y,x,-z
```

```
5 -x,-x+y,-z
```

```
6 x-y,-y,-z
```

7 -x,-y,-z  
8 y,-x+y,-z  
9 x-y,x,-z  
10 -y,-x,z  
11 x,x-y,z  
12 -x+y,y,z  
13 x+1/3,y+2/3,z+2/3  
14 -y+1/3,x-y+2/3,z+2/3  
15 -x+y+1/3,-x+2/3,z+2/3  
16 y+1/3,x+2/3,-z+2/3  
17 -x+1/3,-x+y+2/3,-z+2/3  
18 x-y+1/3,-y+2/3,-z+2/3  
19 -x+1/3,-y+2/3,-z+2/3  
20 y+1/3,-x+y+2/3,-z+2/3  
21 x-y+1/3,x+2/3,-z+2/3  
22 -y+1/3,-x+2/3,z+2/3  
23 x+1/3,x-y+2/3,z+2/3  
24 -x+y+1/3,y+2/3,z+2/3  
25 x+2/3,y+1/3,z+1/3  
26 -y+2/3,x-y+1/3,z+1/3  
27 -x+y+2/3,-x+1/3,z+1/3  
28 y+2/3,x+1/3,-z+1/3  
29 -x+2/3,-x+y+1/3,-z+1/3  
30 x-y+2/3,-y+1/3,-z+1/3  
31 -x+2/3,-y+1/3,-z+1/3  
32 y+2/3,-x+y+1/3,-z+1/3  
33 x-y+2/3,x+1/3,-z+1/3  
34 -y+2/3,-x+1/3,z+1/3  
35 x+2/3,x-y+1/3,z+1/3  
36 -x+y+2/3,y+1/3,z+1/3

loop\_  
\_atom\_site\_label  
\_atom\_site\_type\_symbol  
\_atom\_site\_symmetry\_multiplicity  
\_atom\_site\_Wyckoff\_symbol  
\_atom\_site\_fract\_x  
\_atom\_site\_fract\_y  
\_atom\_site\_fract\_z  
\_atom\_site\_occupancy  
\_atom\_site\_fract\_symmform  
Bi1 Bi 6 c 0.00000 0.00000 0.39658 1.00000 0,0,Dz  
Se1 Se 3 a 0.00000 0.00000 0.00000 1.00000 0,0,0  
Se2 Se 6 c 0.00000 0.00000 0.78071 1.00000 0,0,Dz

# end of cif

```

#=====
# CRYSTAL DATA
#-----
data_Bi15Eu1Se24

_chemical_name_common          'Bi15Eu1Se24'
_cell_length_a                 21.177450
_cell_length_b                 21.177450
_cell_length_c                 21.177450
_cell_angle_alpha               22.840445
_cell_angle_beta                22.840445
_cell_angle_gamma               22.840445
_cell_volume                    1255.734964
_space_group_name_H-M_alt      'P 1'
_space_group_IT_number          1

loop_
_space_group_symop_operation_xyz
'x, y, z'

loop_
_atom_site_label
_atom_site_occupancy
_atom_site_fract_x
_atom_site_fract_y
_atom_site_fract_z
_atom_site_adp_type
_atom_site_U_iso_or_equiv
_atom_site_type_symbol

Bi1    1.0    0.197266   0.201268   0.197266   Uiso ? Bi
Bi2    1.0    0.198225   0.198050   0.698050   Uiso ? Bi
Bi3    1.0    0.198132   0.698132   0.198132   Uiso ? Bi
Bi4    1.0    0.197266   0.697266   0.701268   Uiso ? Bi
Bi5    1.0    0.698050   0.198050   0.198225   Uiso ? Bi
Bi6    1.0    0.701268   0.697266   0.197266   Uiso ? Bi

```

Bi7	1.0	0.698050	0.698225	0.698050	Uiso	? Bi
Bi8	1.0	0.301894	0.302291	0.301894	Uiso	? Bi
Bi9	1.0	0.303171	0.301573	0.801573	Uiso	? Bi
Bi10	1.0	0.301067	0.801067	0.301067	Uiso	? Bi
Bi11	1.0	0.301894	0.801894	0.802291	Uiso	? Bi
Bi12	1.0	0.801573	0.301573	0.303171	Uiso	? Bi
Bi13	1.0	0.802030	0.302030	0.802030	Uiso	? Bi
Bi14	1.0	0.802291	0.801894	0.301894	Uiso	? Bi
Bi15	1.0	0.801573	0.803171	0.801573	Uiso	? Bi
Eu1	1.0	0.696117	0.196117	0.696117	Uiso	? Eu
Se1	1.0	0.000043	0.000301	0.000043	Uiso	? Se
Se2	1.0	0.992021	0.004437	0.504437	Uiso	? Se
Se3	1.0	0.999865	0.499865	0.999865	Uiso	? Se
Se4	1.0	0.000043	0.500043	0.500301	Uiso	? Se
Se5	1.0	0.504437	0.004437	0.992021	Uiso	? Se
Se6	1.0	0.500173	0.000173	0.500173	Uiso	? Se
Se7	1.0	0.500301	0.500043	0.000043	Uiso	? Se
Se8	1.0	0.504437	0.492021	0.504437	Uiso	? Se
Se9	1.0	0.389949	0.390114	0.389949	Uiso	? Se
Se10	1.0	0.391199	0.388077	0.888077	Uiso	? Se
Se11	1.0	0.390141	0.890141	0.390141	Uiso	? Se
Se12	1.0	0.389949	0.889949	0.890114	Uiso	? Se
Se13	1.0	0.888077	0.388077	0.391199	Uiso	? Se
Se14	1.0	0.889985	0.389985	0.889985	Uiso	? Se
Se15	1.0	0.890114	0.889949	0.389949	Uiso	? Se
Se16	1.0	0.888077	0.891199	0.888077	Uiso	? Se
Se17	1.0	0.110629	0.109158	0.110629	Uiso	? Se
Se18	1.0	0.110205	0.110205	0.610205	Uiso	? Se
Se19	1.0	0.110283	0.610283	0.110283	Uiso	? Se
Se20	1.0	0.110629	0.610629	0.609158	Uiso	? Se
Se21	1.0	0.610205	0.110205	0.110205	Uiso	? Se
Se22	1.0	0.610007	0.110007	0.610007	Uiso	? Se
Se23	1.0	0.609158	0.610629	0.110629	Uiso	? Se
Se24	1.0	0.610205	0.610205	0.610205	Uiso	? Se

```

#=====
# CRYSTAL DATA
#-----
data_Bi14Eu2Se24

_chemical_name_common      'Bi14Eu2Se24'
_cell_length_a            21.139488
_cell_length_b            21.139488
_cell_length_c            21.139488
_cell_angle_alpha          22.883610
_cell_angle_beta           22.883610
_cell_angle_gamma          22.883610
_cell_volume                1253.527361
_space_group_name_H-M_alt    'P 1'
_space_group_IT_number        1

loop_
_space_group_symop_operation_xyz
'x, y, z'

loop_
_atom_site_label
_atom_site_occupancy
_atom_site_fract_x
_atom_site_fract_y
_atom_site_fract_z
_atom_site_adp_type
_atom_site_U_iso_or_equiv
_atom_site_type_symbol

Bi1   1.0   0.197284   0.702029   0.197284   Uiso ? Bi
Bi2   1.0   0.197957   0.698185   0.698185   Uiso ? Bi
Bi3   1.0   0.198126   0.198126   0.198126   Uiso ? Bi
Bi4   1.0   0.197284   0.197284   0.702029   Uiso ? Bi
Bi5   1.0   0.698185   0.698185   0.197957   Uiso ? Bi
Bi6   1.0   0.702029   0.197284   0.197284   Uiso ? Bi

```

Bi7	1.0	0.698185	0.197957	0.698185	Uiso	? Bi
Bi8	1.0	0.301815	0.802043	0.301815	Uiso	? Bi
Bi9	1.0	0.297971	0.802716	0.802716	Uiso	? Bi
Bi10	1.0	0.301815	0.301815	0.802043	Uiso	? Bi
Bi11	1.0	0.802716	0.802716	0.297971	Uiso	? Bi
Bi12	1.0	0.801874	0.801874	0.801874	Uiso	? Bi
Bi13	1.0	0.802043	0.301815	0.301815	Uiso	? Bi
Bi14	1.0	0.802716	0.297971	0.802716	Uiso	? Bi
Eu1	1.0	0.695502	0.695502	0.695502	Uiso	? Eu
Eu2	1.0	0.304498	0.304498	0.304498	Uiso	? Eu
Se1	1.0	0.000000	0.500000	0.000000	Uiso	? Se
Se2	1.0	0.000000	0.500000	0.500000	Uiso	? Se
Se3	1.0	0.000000	0.000000	0.000000	Uiso	? Se
Se4	1.0	0.000000	0.000000	0.500000	Uiso	? Se
Se5	1.0	0.500000	0.500000	0.000000	Uiso	? Se
Se6	1.0	0.500000	0.500000	0.500000	Uiso	? Se
Se7	1.0	0.500000	0.000000	0.000000	Uiso	? Se
Se8	1.0	0.500000	0.000000	0.500000	Uiso	? Se
Se9	1.0	0.389954	0.890146	0.389954	Uiso	? Se
Se10	1.0	0.394979	0.886181	0.886181	Uiso	? Se
Se11	1.0	0.390495	0.390495	0.390495	Uiso	? Se
Se12	1.0	0.389954	0.389954	0.890146	Uiso	? Se
Se13	1.0	0.886181	0.886181	0.394979	Uiso	? Se
Se14	1.0	0.889911	0.889911	0.889911	Uiso	? Se
Se15	1.0	0.890146	0.389954	0.389954	Uiso	? Se
Se16	1.0	0.886181	0.394979	0.886181	Uiso	? Se
Se17	1.0	0.113819	0.605021	0.113819	Uiso	? Se
Se18	1.0	0.109854	0.610046	0.610046	Uiso	? Se
Se19	1.0	0.110089	0.110089	0.110089	Uiso	? Se
Se20	1.0	0.113819	0.113819	0.605021	Uiso	? Se
Se21	1.0	0.610046	0.610046	0.109854	Uiso	? Se
Se22	1.0	0.609505	0.609505	0.609505	Uiso	? Se
Se23	1.0	0.605021	0.113819	0.113819	Uiso	? Se
Se24	1.0	0.610046	0.109854	0.610046	Uiso	? Se

