

# **Magnetoelectric coupling in the type-I multiferroic $\text{ScFeO}_3$**

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# What is a type-I multiferroic?

Multiferroics are

- materials exhibiting coexistence of multiple ferroic orders (FE and magnetism in our case)
- classified according to the origin of these coexisting ferroic orders.

## ***Type-I Multiferroics***

- Ferroelectricity and magnetism originate from different atomic sublattices
- Thus, FE and magnetism are largely independent of each other
- However, the possibility of coupling between FE and magnetism remains
- $BiFeO_3$  and  $Sr_{1-x}Ba_xMnO_3$  (high magnetic ordering temperatures and large FE polarizations)

## ***Type-II Multiferroics***

- Magnetism induces ferroelectricity
- Implying strong coupling between FE and magnetic order
- $RMnO_3$  and  $RMn_2O_5$  (magnetic structure lifts inversion symmetry and gives rise to FE distortion)

# Type-I multiferroic $ScFeO_3$

## *High pressure $ScFeO_3$*

Prepared under 15 GPa at temperatures above 1100K

High pressure phase exhibits a polar  $R3c$  space group.

Consists of highly distorted  $ScO_6$  and  $FeO_6$  octahedral

Exhibits a weak ferromagnetism with high magnetic ordering temperature 545K

Canted G-type antiferromagnetic ordering of  $Fe^{3+}$  ions

## *$h-RFeO_3$*

Fundamentally different from our thin film growth process

Compare this with  $P6_3cm$  space group of  $h-RFeO_3$

$Fe^{3+}$  ions are placed in trigonal bipyramid environment and coordination of  $R^{3+}$  ions is debatable.

Exhibits a weak ferromagnetism with magnetic ordering temperatures in the range 120 – 150K

# Type-I multiferroic $ScFeO_3$

- Shares the same R3c space group as  $LiNbO_3$  and  $BiFeO_3$
- displays a “mixture “ of electronic and FE properties of  $LiNbO_3$  and  $BiFeO_3$

$ScFeO_3$  is similar to  $LiNbO_3$  as in

- the A site in  $ScFeO_3$  is severely under-bonded
- FE distortion involving the A cation is needed to stabilize the structure and optimize the environment of the A site

In  $LiNbO_3$

- The B site is non-magnetic

In  $BiFeO_3$ ,

- FE distortion stems from the stereochemical activity of the  $6s^2$  lone pair of  $Bi^{3+}$  cation

$ScFeO_3$  is similar to  $BiFeO_3$  as in

- The B site in  $ScFeO_3$  is magnetic like  $BiFeO_3$
- Has high magnetic ordering temperature like  $BiFeO_3$ ,  $Sr_{1-x}Ba_xMnO_3$ , and  $PbNiO_3$

Thus,  $ScFeO_3$  is a type-I multiferroic where both FE and magnetic order exist  
Albeit expected to be **weakly** coupled

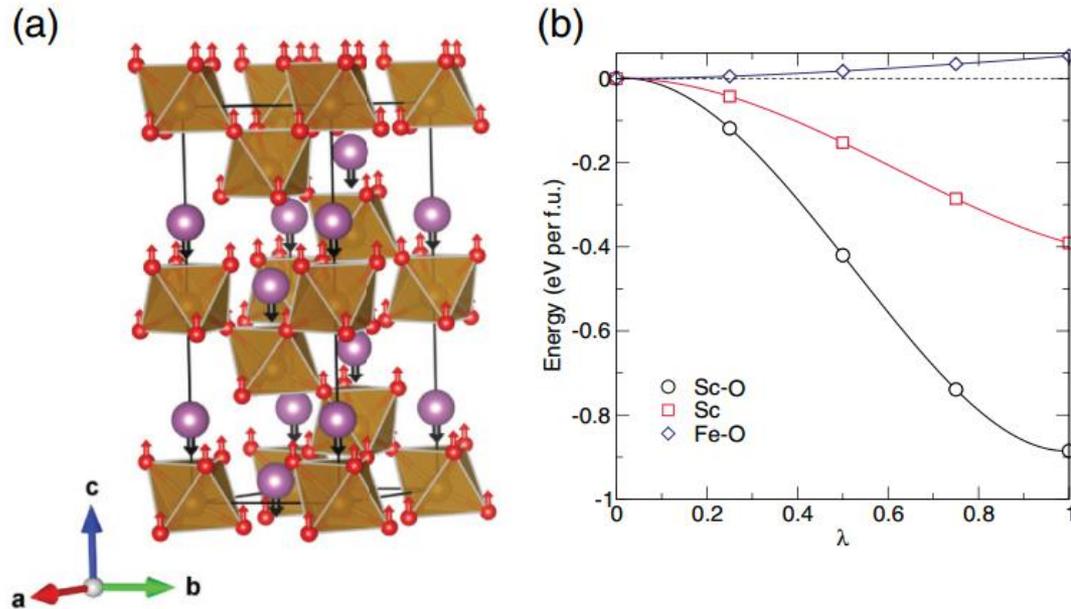
# Theoretical study of multiferroic $ScFeO_3$

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- Theoretical estimate of the Neel temperature is 635K
- Large FE polarization of  $\sim 105 \text{ uC/cm}^2$
- Authors examine the dependence of polarization on the magnetic order
  - They find evidence of strong magnetoelectric coupling between the local Fe magnetization and the ***electronic contribution*** to the total electric polarization

# Theoretical study of multiferroic $ScFeO_3$

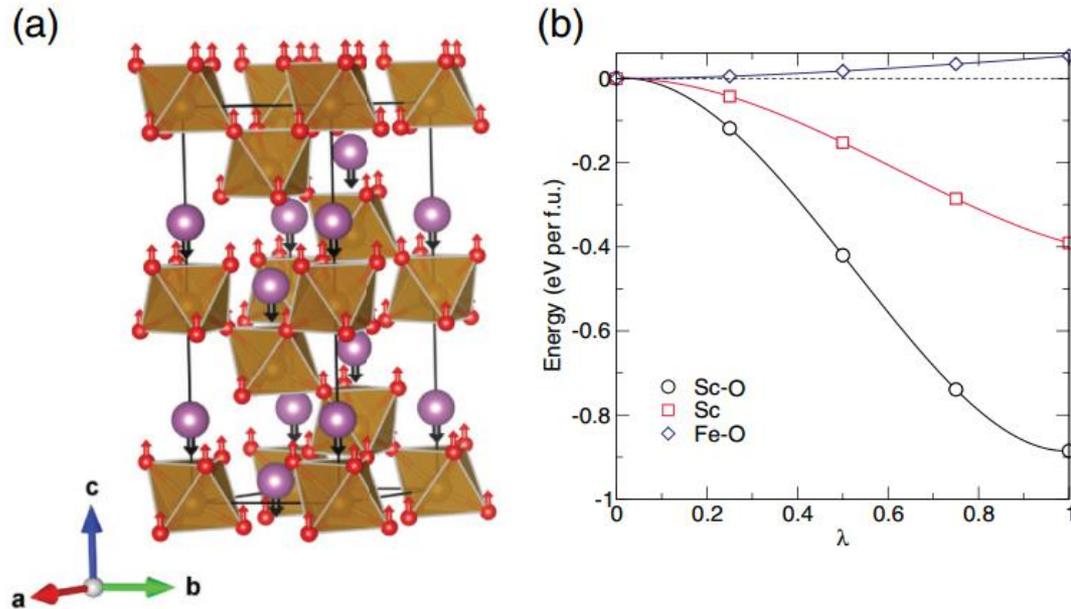
## Structural Aspects



- The figure depicts the polar displacements of the Sc and O ions in the  $R3c$  crystal structure.
- These displacements are along the  $[111]$  pseudocubic direction.
- This results in a spontaneous polarization along the  $c$  axis in the hexagonal setting of the rhombohedral structure
- The geometry-induced inversion symmetry breaking of the  $R3c$  structure with respect to the centrosymmetric  $R-3c$  phase can be described by a polar mode with  $A^{2u}$  symmetry.

# Theoretical study of multiferroic $ScFeO_3$

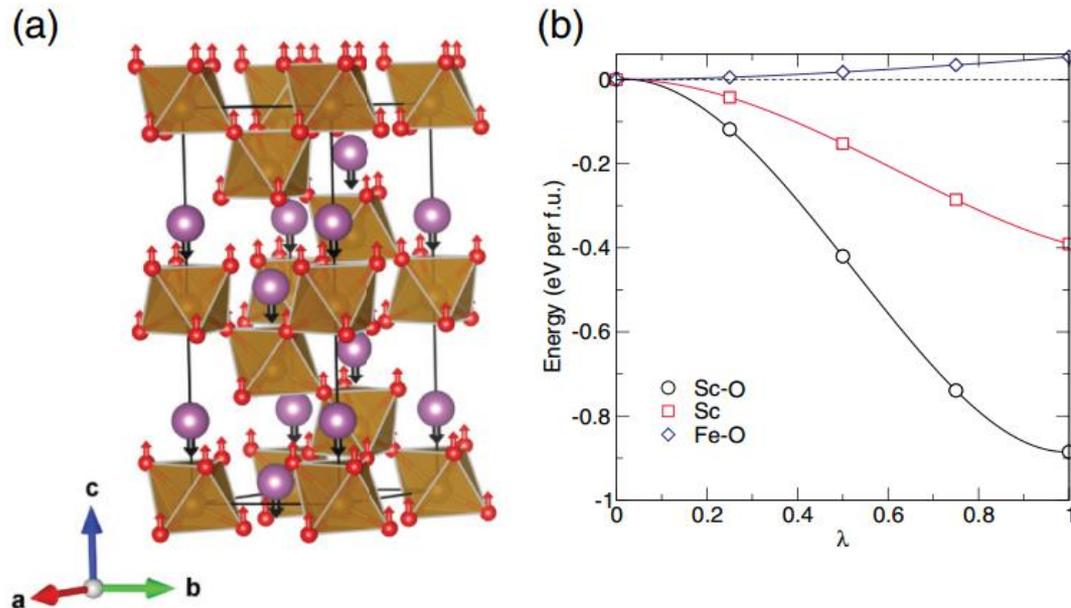
## Structural Aspects



- Along the polar  $c$  axis, the Sc and O ions have opposite displacements of -0.55 and 0.29 Å, respectively
- Fe cations undergo minor displacements and contribute weakly to the electric polarization
- Along the nonpolar  $a$  and  $b$  axes, the Sc and O ions exhibit antipolar displacements.

# Theoretical study of multiferroic $ScFeO_3$

## *Energetics physical properties and structure*



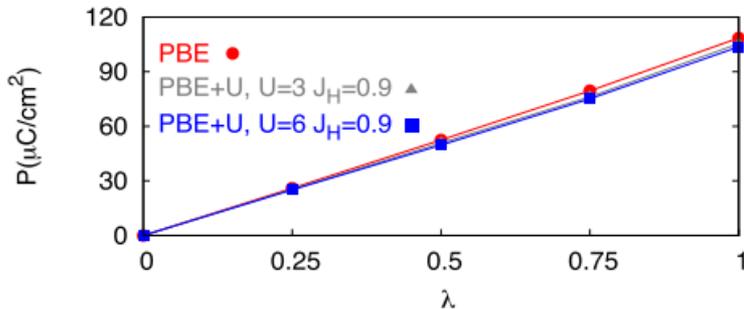
- The energy gain ( $dE$ ) of the polar  $R3c$  structure with respect to the centrosymmetric  $R-3c$  structure obtained by displacing the Sc and O (Sc-O) ions, Sc cation only and the Fe and O (Fe-O) ions **in the  $A_{2u}$  mode**

$\lambda$  is a dimensionless parameter that continuously connects the centrosymmetric  $R-3c$  structure ( $\lambda = 0$ ) to the experimentally determined polar  $R3c$  structure ( $\lambda = 1$ ).

- The  $R3c$  structure is stabilized by either displacing the Sc cation or the Sc-O ions
- Fe-O distortions alone are unfavorable

# Theoretical study of multiferroic $ScFeO_3$

## *Energetics physical properties and structure*



Total ferroelectric polarization  $P$  as a function of the Sc-O displacement mode.

Born effective charges ( $Z^*$ ) for the  $R3c$  structure of  $ScFeO_3$  as a function of the different levels.

	Sc (+3)	Fe (+3)	O (-2)
PBE	3.815	3.688	-2.505
PBE + $U = 3$ eV	3.798	3.650	-2.477
PBE + $U = 6$ eV	3.780	3.504	-2.433

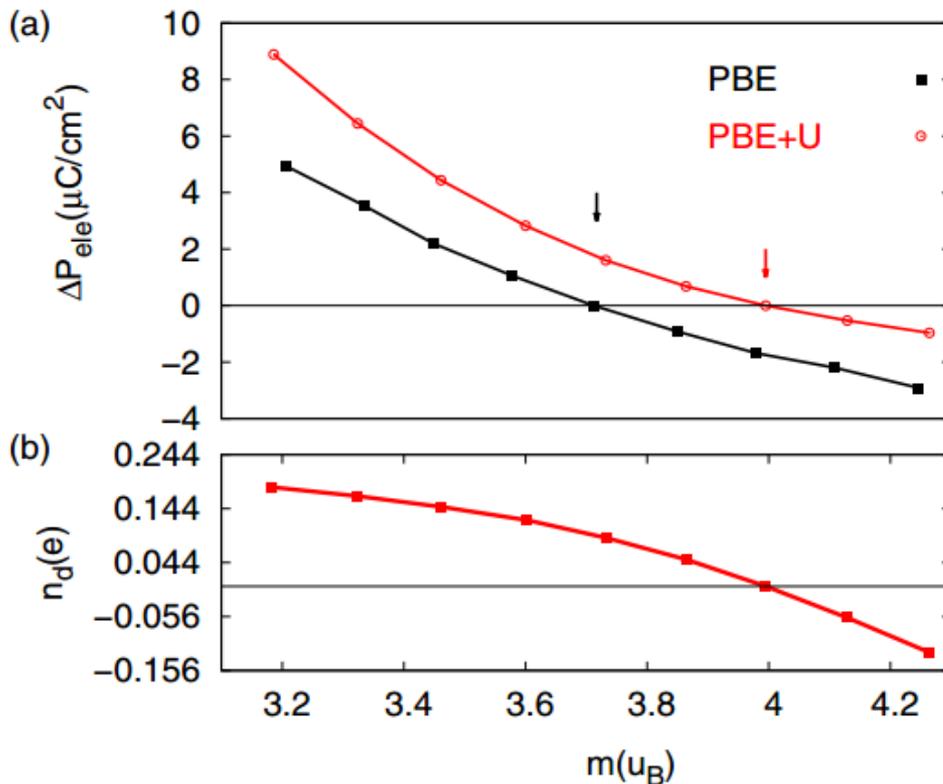
- $Z^*$  of Sc is somewhat larger than the nominal oxidation state, indicating the importance of this ion in the polar distortion.
- This is similar to  $BiFeO_3$  but different from  $LiNbO_3$  where the  $Z^*$  of the A cations are much closer to the nominal values.

**Ferroelectric polarization is mainly driven by the Sc and O atoms**

# Theoretical study of multiferroic $ScFeO_3$

## Magnetoelectric coupling

- Use the experimental  $R3c$  crystal structure to evaluate the *electronic* contribution to the **ferroelectric polarization** (sum of the electronic and ionic contributions) as a function of the amplitude of the local Fe magnetic moment.



(a) Change of the electronic contribution ( $\Delta P_{ele}$ ) to ferroelectric polarization for  $ScFeO_3$  as a function of local Fe moment

(b) Change of Fe charge as a function of the local Fe magnetization at fixed experimental ionic positions.

# Conclusions

- The A site in  $\text{ScFeO}_3$  is under-bonded. This induces non-centrosymmetric FE distortion involving the A cation to stabilize the structure and optimize the environment of the A site
- The FE in high pressure phase  $\text{ScFeO}_3$  arises through Sc and O ion. The anions play an important role in FE distortions.
- Theoretically, the net polarization depends strongly upon the magnetic moment of local Fe ions.

***Thank you!***