Understanding of microscopic origin of polarization and magnetoelectric coupling in Fe_2TeO_6

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Abstract

We present the rare existence of d^5 off-centering induced weak ferroelectric polarization and and magnetoelectric (ME) properties in the G type (T_N~210 K) antiferromagnet Fe_2TeO_6 (FTO) compound. The origin of ferroelectricity (FE) is associated with both lattice and asymmetric electron density distribution around the ion cores. ME coupling is observed in magnetic field-dependent polarization, ME voltage, and magnetostrain measurements. Short-range magnetic ordering due to intrabilayer dimeric exchange coupling via the double oxygen bridged Fe-O1-Fe pathway is proposed to play a dominating role to exhibit the negative nonlinear magnetic field dependent ME behavior at 300 K. Interbilayer exchange via Fe-O2-Fe pathways dominantly determines the hysteretic nonlinear magnetic field dependent ME response below T_N. The observed nonlinear ME coupling signifies magnetoelasticity as manifested in the temperature and magnetic field-dependent strain measurement. Hence the rare existence of FE and magnetoelectric coupling by d^5 ion is presented in FTO.

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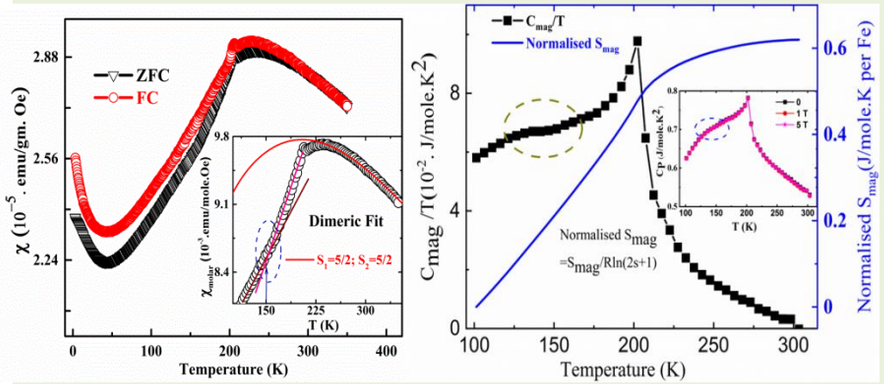
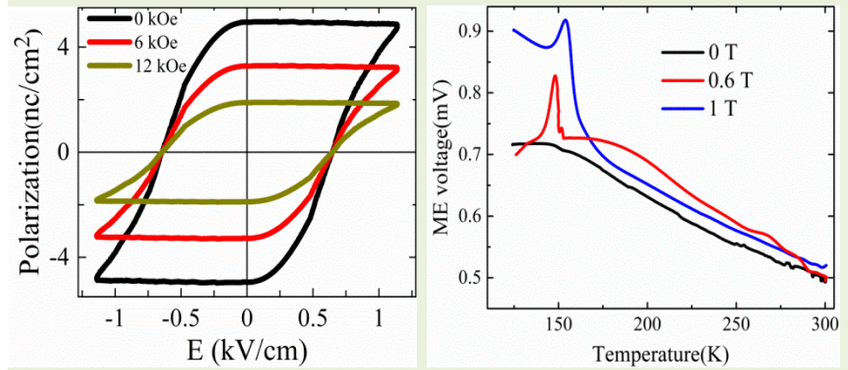
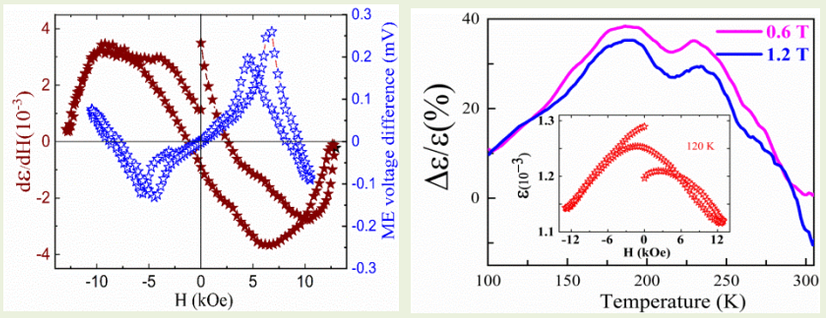
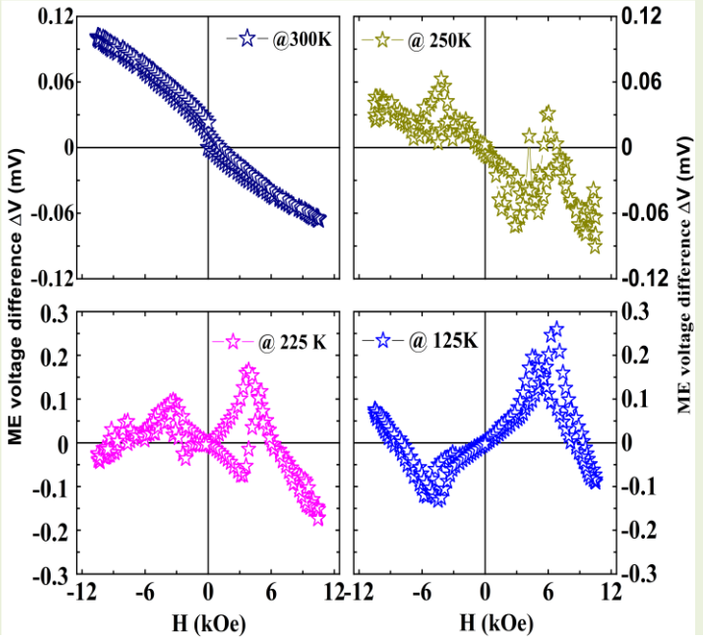
Macrosopic magnetic and magnetoelectric properties





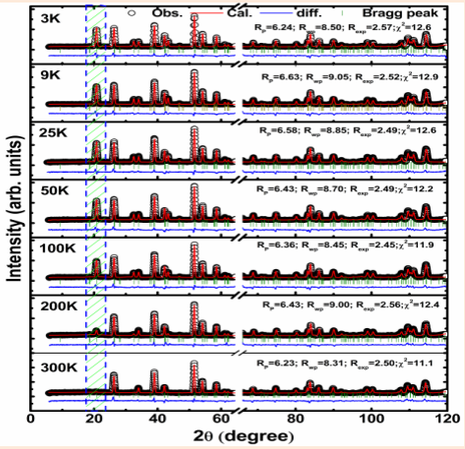


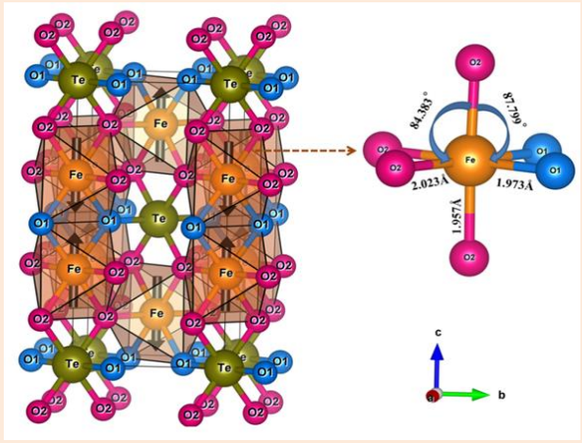
- T_N~210 K,
- 5/2-5/2 dimeric interaction: Magnetic correlation above T_N
- Direct evidences of magnetoelectric (ME) Coupling; Direct Measurements:
  - Polarization vs Electric field under magntiec field at 300 K (RT)
  - ME voltage : Different kind of ME coupling at $T_N < T < T_N$
  - Magnetostrain: Magnetoelastic coupling

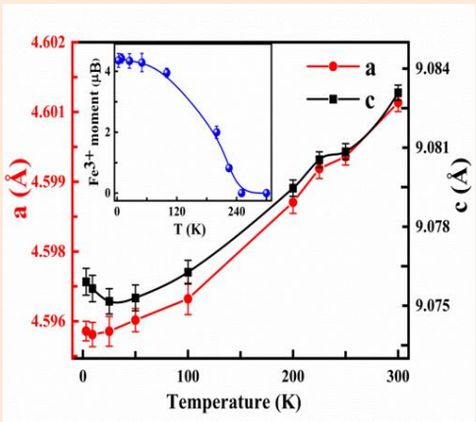


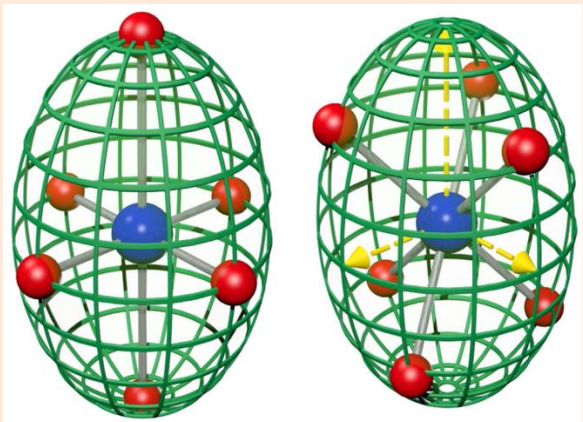
Microscopic understanding of ferroelectricity and ME coupling

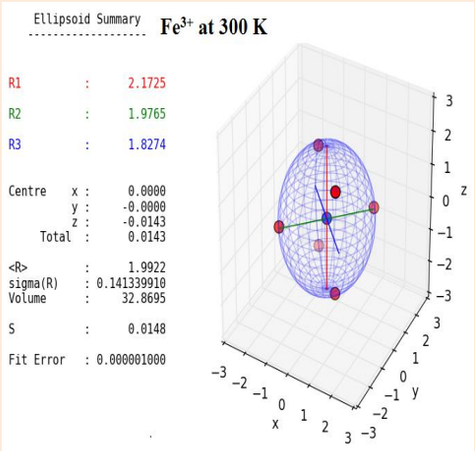
Neutron diffraction study and Ellipsoid analysis











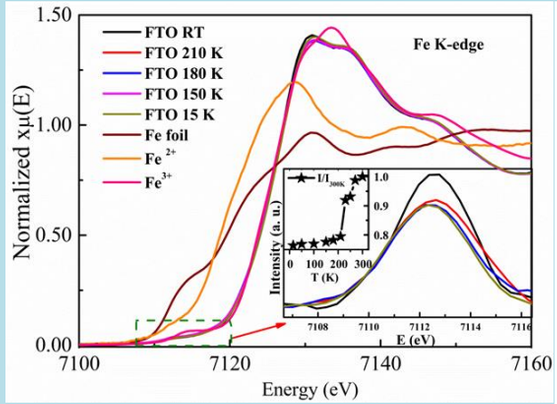
Fitting the coordination polyhedra with : Minimum Bounding Ellipsoid (MBE) :Bond distortion &Angular distortion [1]

i) Principal radii; R_1, R_2, R_3 ($R_1 \geq R_2 \geq R_3$)
ii) d: Central cationic displacement
iii) <R>: Mean radius; Size
iv) $\sqrt{\sigma^2(R)}$; Variance: distortion
v) $S=(R_3/R_2-R_2/R_1)$: S<0: Oblate, S>0: Prolate, S=0: Sphere

- *Reduced (13%) moment of Fe^{3+}; 4.35 μ_B*
- *d^5 off centering of Fe^{3+}*
- *Deviation from D_{4h} symmetry*
- *Change in polyhedra shape and size at T_N: Magnetostructural correlation*
- *Nonmonotonic temperature variation of distortion*
- *Non-octahedral hybridization*

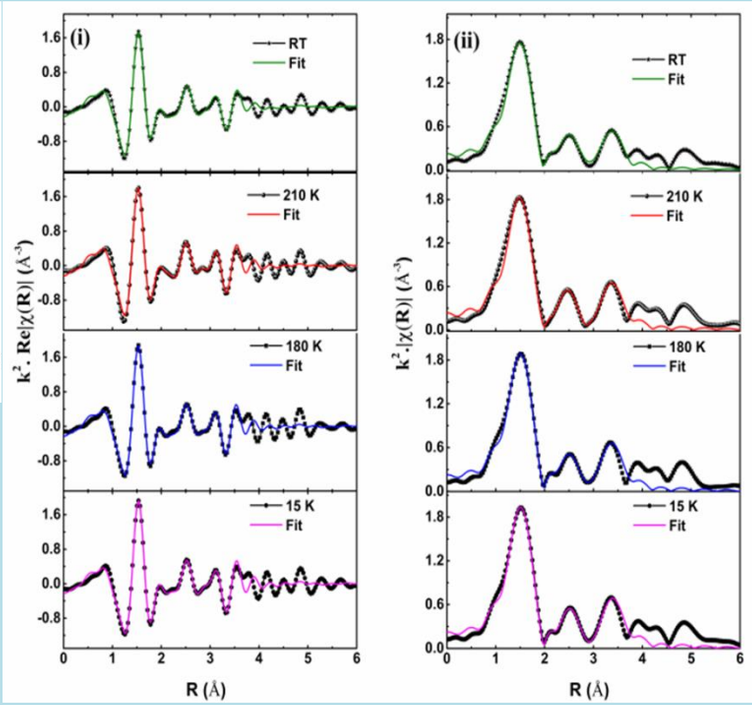
X-ray Absorption Spectroscopy

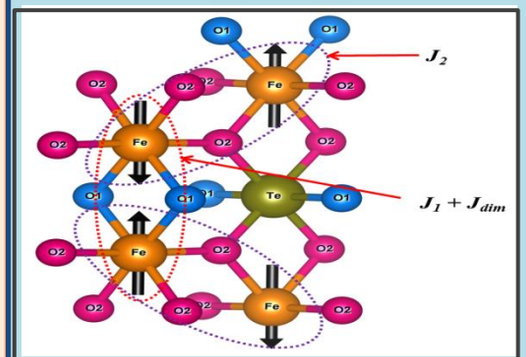
XANE: X-ray near edge spectra



- **Fe K edge confirms existence of *Fe^3***
- **Low intense Gaussian peak; Small deviation from D_{4h} symmetry**
- **Sudden fall in pre-edge intensity at 210 K ; Fe-O hybridization depends upon magnetic correlation [2, 3]**

EXAFS: Extended X-ray absorption fine structure





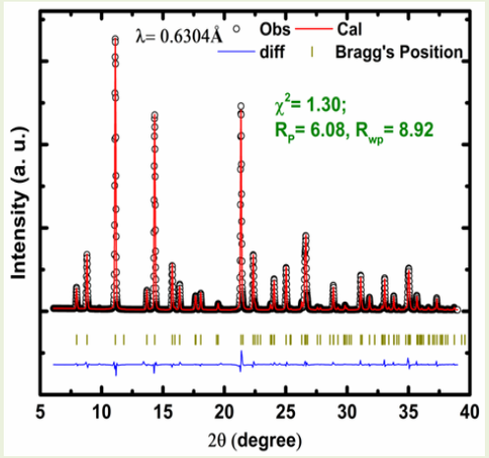
$$\chi(E) = \sum_j \frac{N_j}{kR_j} |f_j(k)| \, e^{-\frac{R_j}{\lambda_e}} e^{-2k^2\sigma_j^2} \sin(2kR_j + 2\delta_1 + \arg(f_j(k)))$$

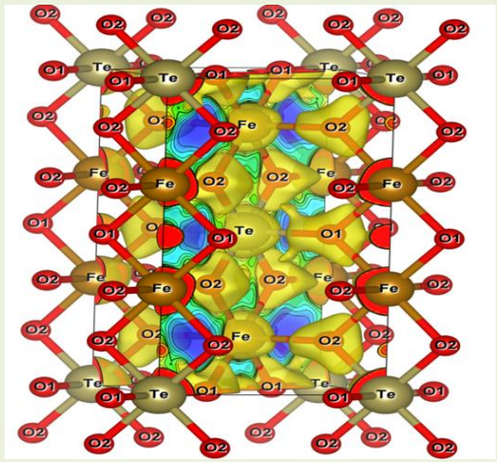
N_j: Coordination Number, R_j: Distance between scatterer & absorber, σ_j : Debye Waller factor; Represent disorder or deviation

- *First coordination cell : D_{4h} symmetry and $P4_2/mnm$*
- *Fe-O (Apical) : 1.995(3) and σ^2 (Å^2): 0.0042*
- *Fe-O2 (Equatorial): 2.0032 ; σ^2 (Å^2): 0.006(3)*
- *Second coordination Fe-O: 3.795 (3) ; large σ^2 (Å^2): 0.0073 implies larger flexibility* **[4, 5]**

Microscopic understanding of ferroelectricity and ME coupling

Charge density distribution calculation : MEM analysis



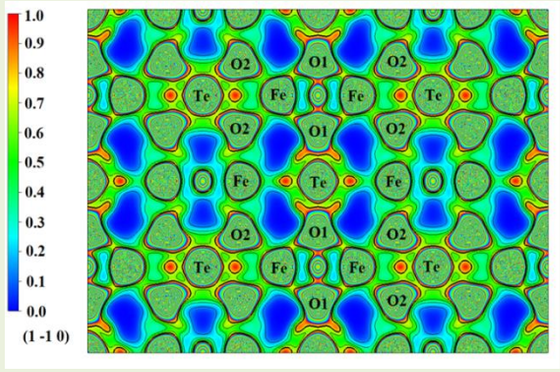


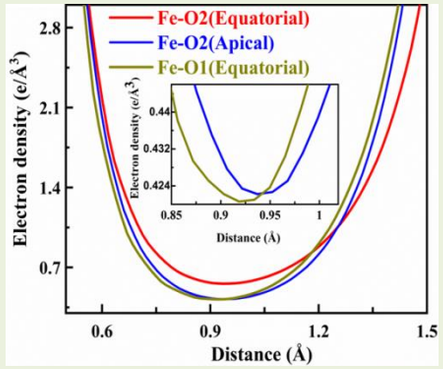
$$F(h) = \sum_r \rho(r) e^{-(2i\pi h.r)}$$

$$\rho(r) = \sum_h F_h e^{(2i\pi h.r)}$$

Conventional Fourier method : Limited number of structure factor

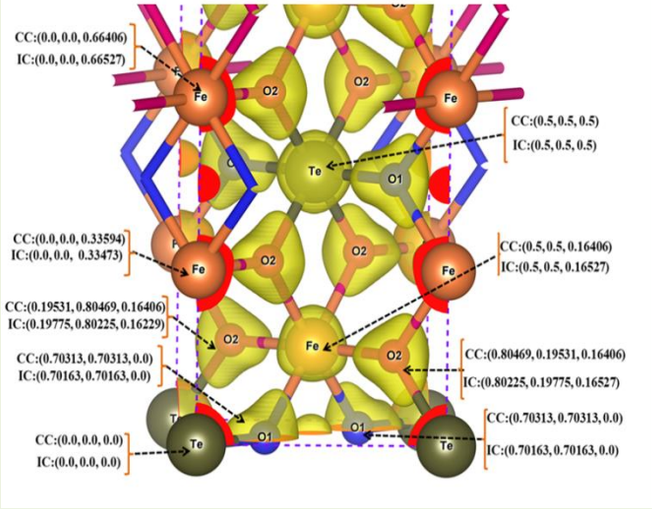
- **Unphysical negative density due to erroneous termination of calculation [6, 7]**





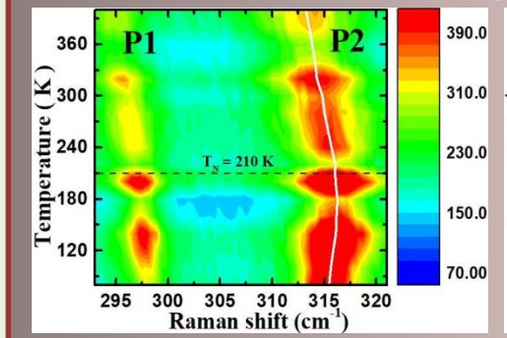
Maximum Entropy Method : MEM analysis

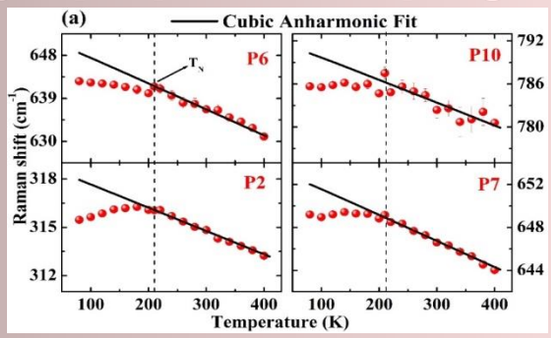
- **1d electron density : different Fe-O bonds**
- **Saddle point and density at saddle point are different**
- **Distortion in Fe^{3+} polyhedra**



- ***Positions of the ionic centers (IC) and the charge cloud centers (CC) : Non-overlapping : ferroelectric polarization***
- ***Microscopic polarization is estimated from the shift (Δc) of each IC and CC center***
- $P = \frac{ne\Delta c}{V}$ ***; n is the number of electrons, e is the electronic charge, and V is the volume of the unit cell.***
- ***Electronic polarization P~ 0.05 μC/cm^{-2}***

Raman spectroscopy: Spin phonon coupling





$$\omega_{anh}(T) = \omega(0) + C\left[1 + \frac{2}{e^{\frac{\hbar\omega}{2kT}} - 1}\right] \qquad \Delta\omega_{sp\_ph} = \omega_{exp}(T - \omega_{anh}(T) = \lambda_{sp} \langle S_i . S_j \rangle \text{ [8]}$$

✓ *Unequal Fe-O2 bond lengths of the Fe-O2-Fe unit give rise to asymmetric vibrations of phonon modes.*

Conclusion

- *AFM ordering below 210 K : Sublattice moment ~4.35μ_B (reduced by ~ 13%)*
- *Finite d^5 off-centering with the non D_{4h} symmetry in Fe^{3+} polyhedra.*
- *The shape, size, and off-centering displacement of Fe^{3+} varies non-monotonically and follow the magnetic transition*
- *Non-octahedral type of hybridization in Fe^{3+} polyhedra.*
- *Dependence of p-d hybridization on magnetic ordering*
- *Asymmetric electron density around the Fe^{3+} is realized. Hence the local distortion in Fe^{3+} is verified*
- *So both d^5 off-centering of Fe^{3+} along with electronic contribution result in finite polarization ~0.05 μC/cm^2*

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References

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