Phonon softening in (Eu,Ba)TiO_3

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Outline

- Search for a permanent electric dipole moment of the electron

  (Supersymmetric extensions to the Standard Model)

- Solid-state experiments

- Ferroelectric material $Eu_{0.5}Ba_{0.5}TiO_3$ (Perovskites)

Electric dipole moment

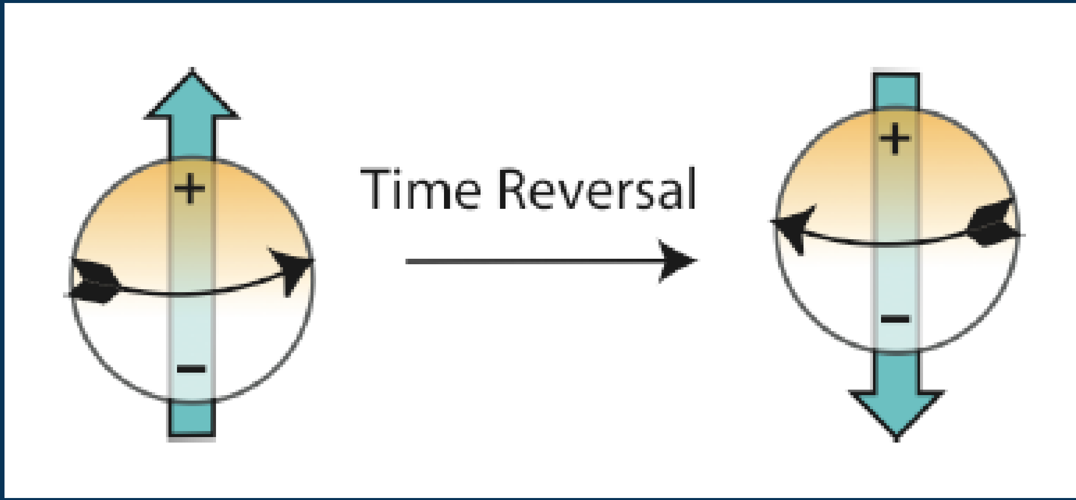
$$p = qd$$

Standard Model says the electron is a point-particle

d = ???

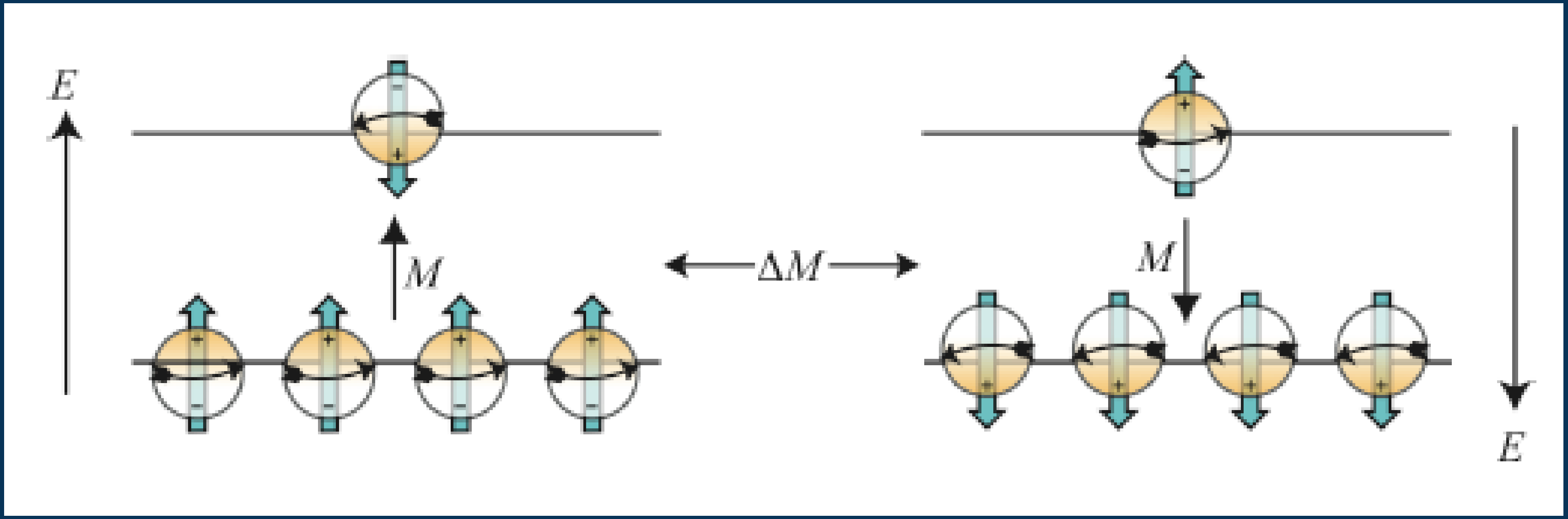
Electric dipole moment

- Time-reversal violation if the EDM exists
- Magnetic dipole reversed but electric dipole is not !
- T-violation implies CP-violation ("CPT theorem")



Blue arrow = magnetic moment
Orange shading = electric dipole moment

EDM measurement



Reverse the E field and measure ΔM

Rushchanski et al, Nature Materials 9, 649 (2010)

Experimental Details

- Ball-mill Eu_2O_3 + TiO_2 + $BaTiO_3$
- XRD, $\chi_{ac,}$ neutron diffraction, ^{151}Eu Mössbauer
- Permittivity

Phonon softening --- Mössbauer

- Cochran, Anderson 1960: occurrence of instabilities in the phonon modes

- Muzikar et al. 1963: connection between Mössbauer f-factor and the T-dependent phonon mode responsible for the displacement Ferroelectricity

$$\langle x^2 \rangle \uparrow$$

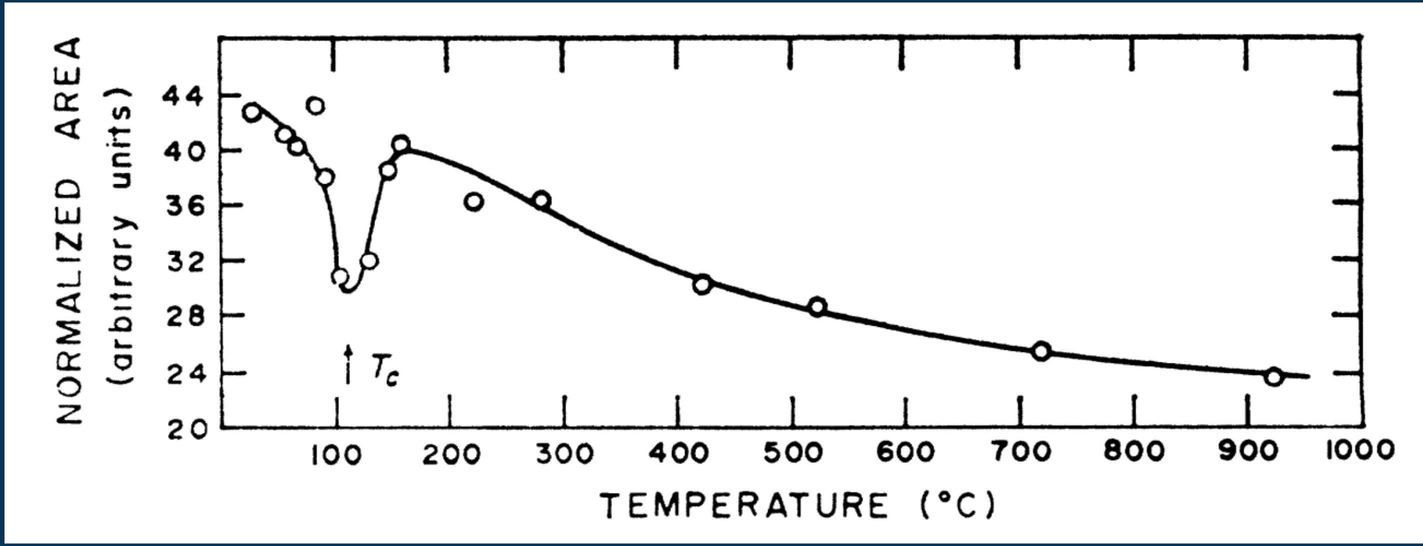
$$f \propto \exp\left(-c\langle x^2 \rangle\right) \downarrow$$

Phonon softening --Mössbauer

PHYSICAL REVIEW VOLUME 139, NUMBER 6A 13 SEPTEMBER 1965

Mössbauer Effect in Ferroelectric $BaTiO_3$†

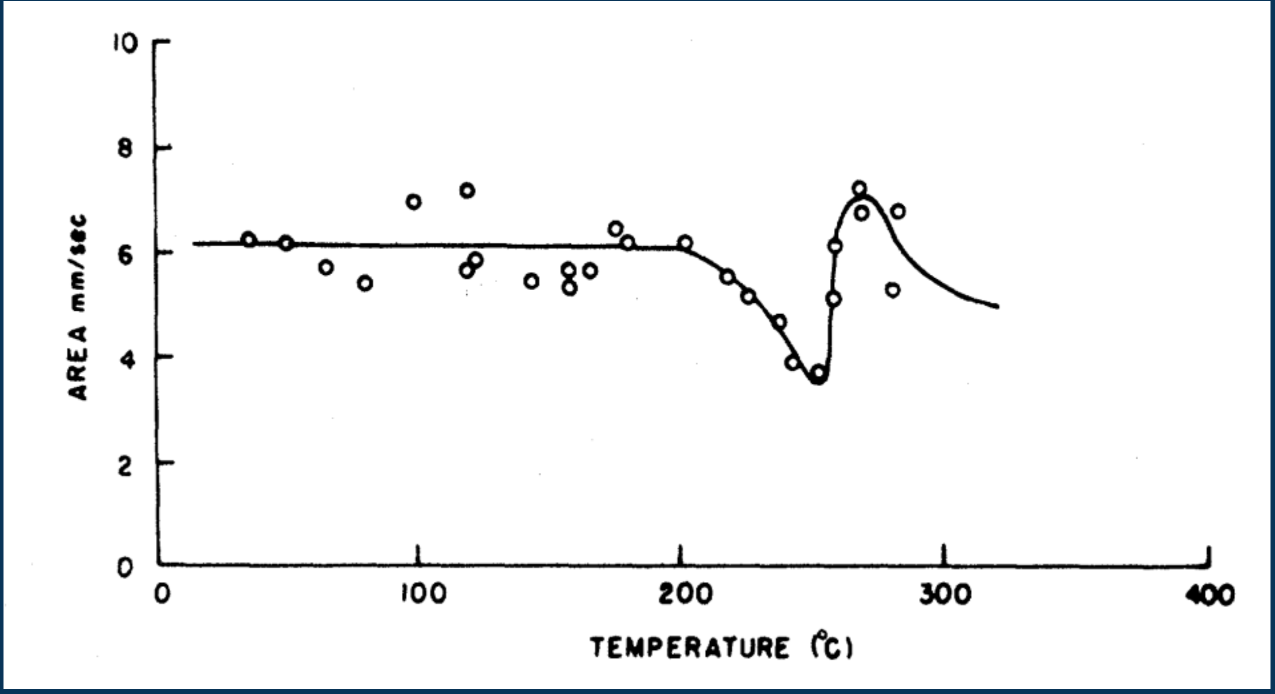
V. G. Bhide and M. S. Multani
Department of Physics, Institute of Science, Bombay, India
(Received 22 March 1965)



PHYSICAL REVIEW B VOLUME 2, NUMBER 7 1 OCTOBER 1970

Temperature-Dependent Optical Mode in Antiferroelectric $PbZrO_3$ by the Mössbauer Effect

A. P. Jain, S. N. Shringi,* and M. L. Sharma
National Physical Laboratory, New Delhi, 12 India
(Received 8 April 1970)

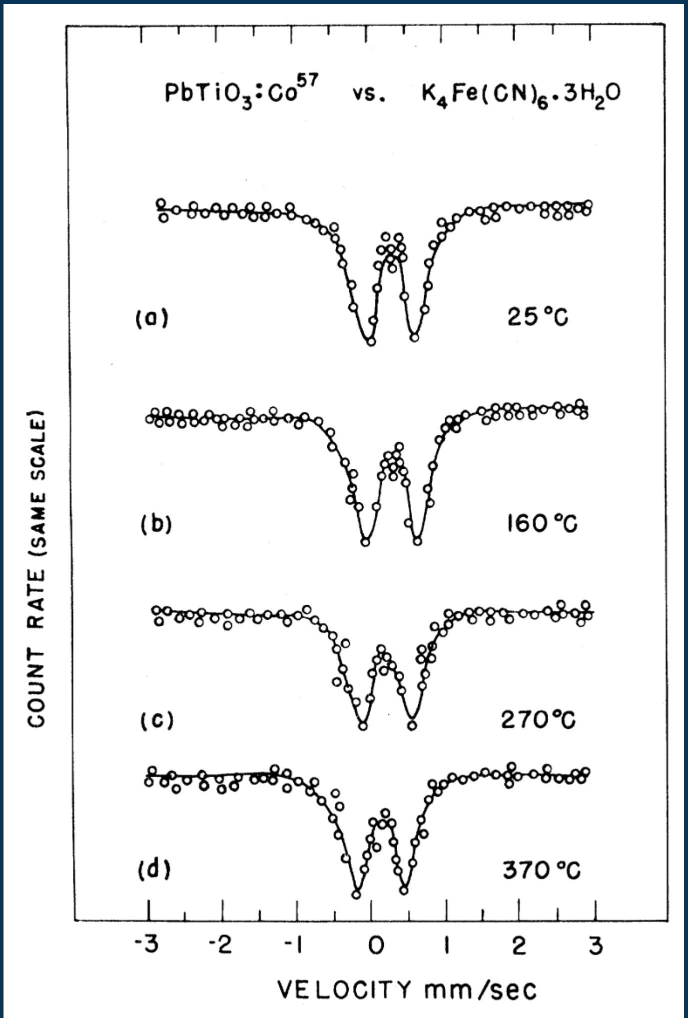


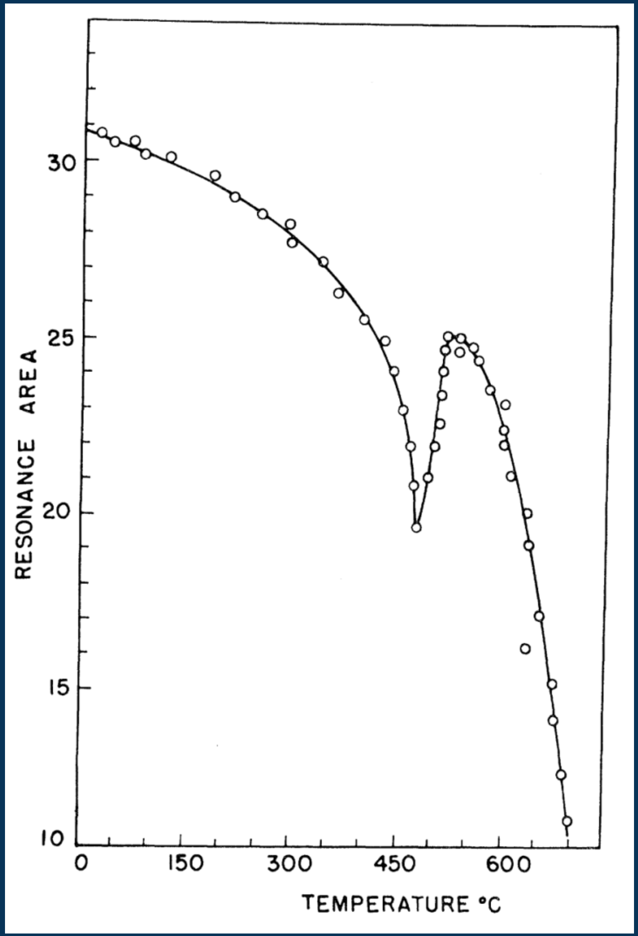
PHYSICAL REVIEW B VOLUME 5, NUMBER 9 1 MAY 1972

Mössbauer Effect for Fe^{57} in Ferroelectric Lead Titanate

V. G. Bhide and M. S. Hegde
National Physical Laboratory, New Delhi-12, India

(Received 2 June 1971)





Materials for EDM search

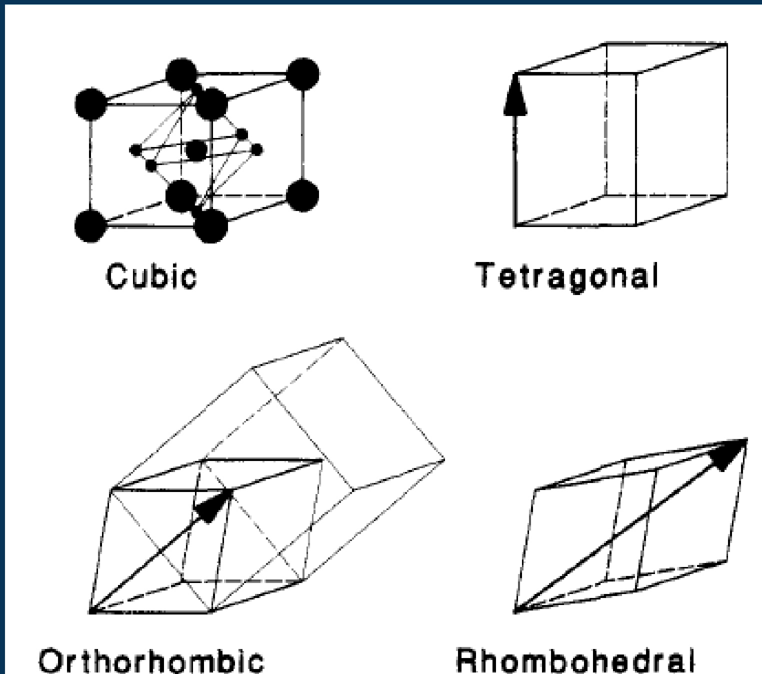
What kind of material do you need ?

- Ferroelectric with a large electric polarization switchable at low-T (4 K) ⟶ TM with a d^0 configuration
- FE enhances the effective E field on the magnetic electrons
- High concentration of ions with a local magnetic moment that remains paramagnetic at 4 K. ⟶ RE 4f localized electrons
- Local environment of each magnetic ion should be strongly modified by the Ferroelectricity

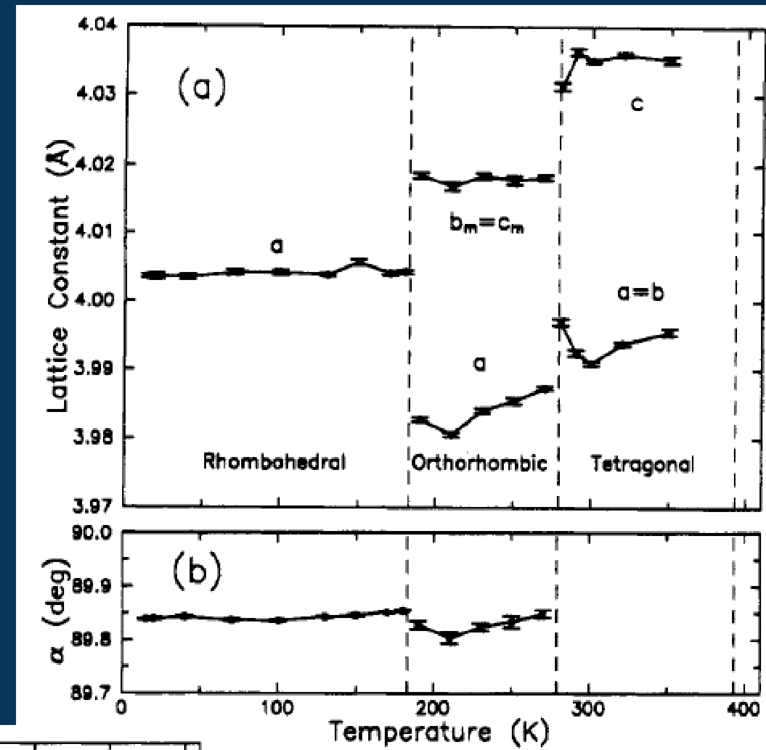
- **$BaTiO_3$**
- Large RT electric polarization (25 μC/cm^2)
- Ba^{2+} has an inert gas electron configuration so magnetic moment = 0
- a = 3.996 Å at RT

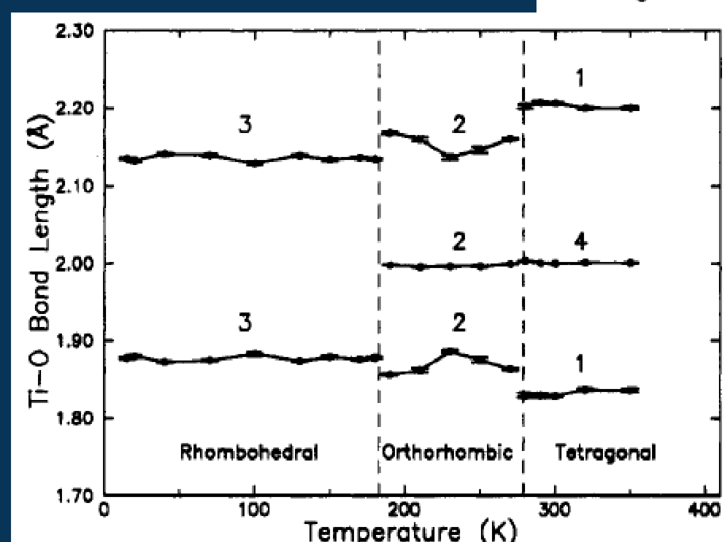
- **$EuTiO_3$**
- Eu^{2+} magnetic $4f^{7}$
- Not ferroelectric but dielectric constant is large (400) at low-T so ‘almost’
- T_N = 5.3 K G-type AF
- Permittivity decreases below T_N but increases in an externally applied B field
- a = 3.905 Å at RT

Ferroelectric transitions in $BaTiO_3$



Pm3m
393K
P4/mmm
278K
Amm2
183K
R3m

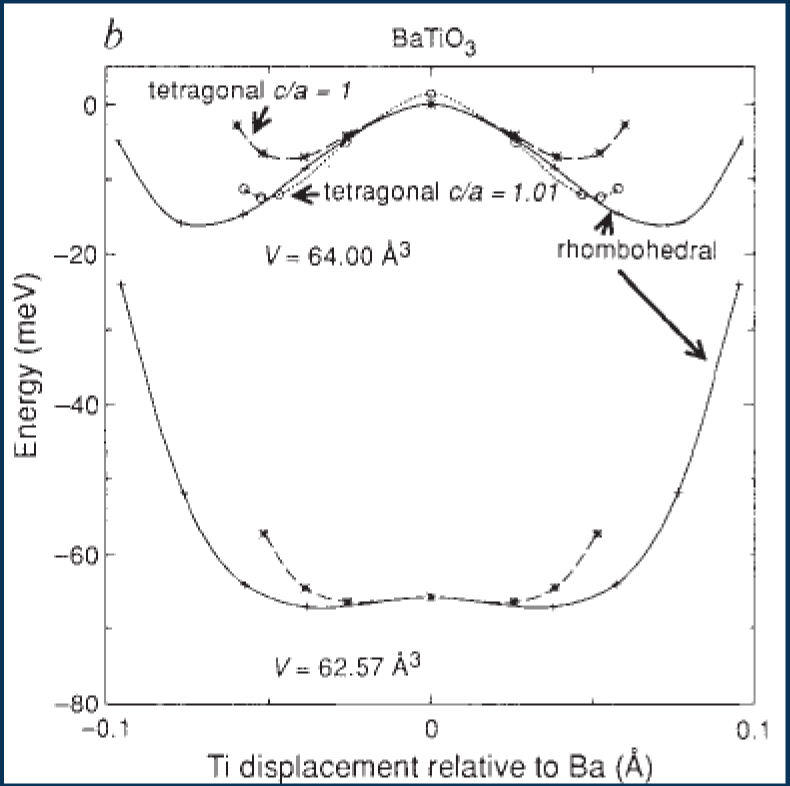




Kwei et al. J.Phys.Chem. 97 2368 (1993)

$BaTiO_3$

- Cochran, Anderson 1960
- Phonon-softening
- Relative ionic displacement
- Cohen 1992
- Hybridization between Oxygen p-states and the empty Ti d-states
- Competition between covalent and ionic forces
- O^{2-} and Ti^{4+}

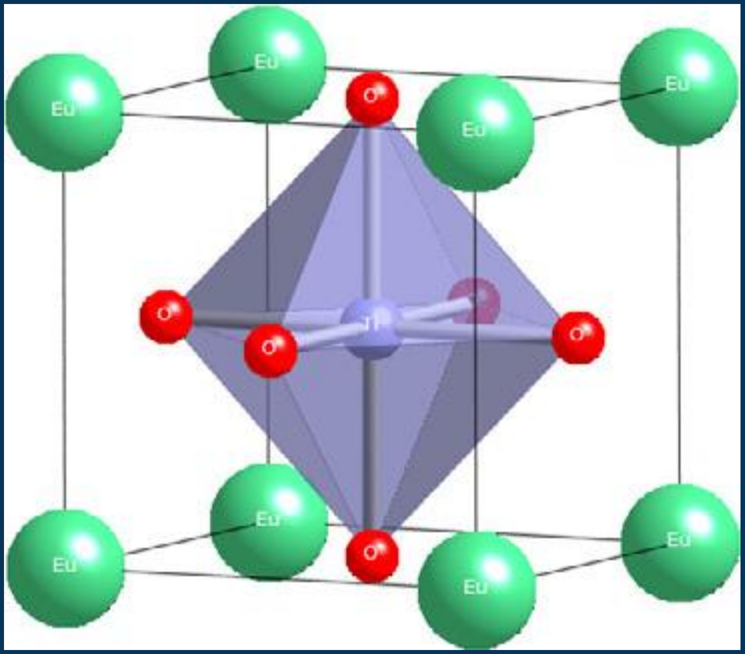


Cohen Nature 358 136 (1992)

$Eu_{0.5}Ba_{0.5}TiO_3$

Crystal Structure

- Perovskite
- Cubic (above 178 K) Pm3m
- a ~ 4.0 Å



Eu,

Ba

O^{2-}

Ti^{4+}

Ranjan et al JPCM 2009

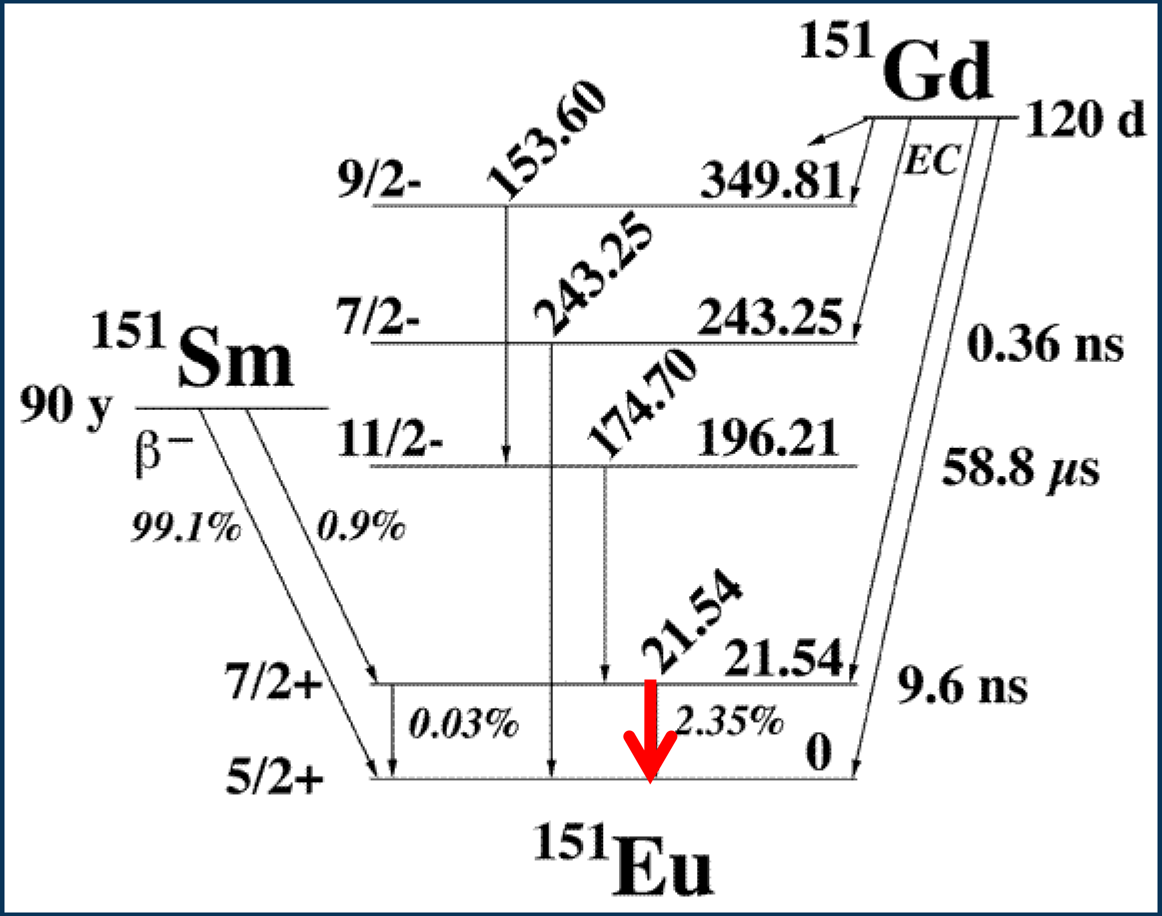
$Eu_{0.5}Ba_{0.5}TiO_3$

- Ba dilution reduces T_N below 2 K.
- Predicted EDM sensitivity is 1.5 x 10^{-28} e-cm after 10 d of averaging (a factor of 10 better than current limit)
- Present experimental upper limit is 1.6 x 10^{-27} e-cm

^{151}Eu Mössbauer

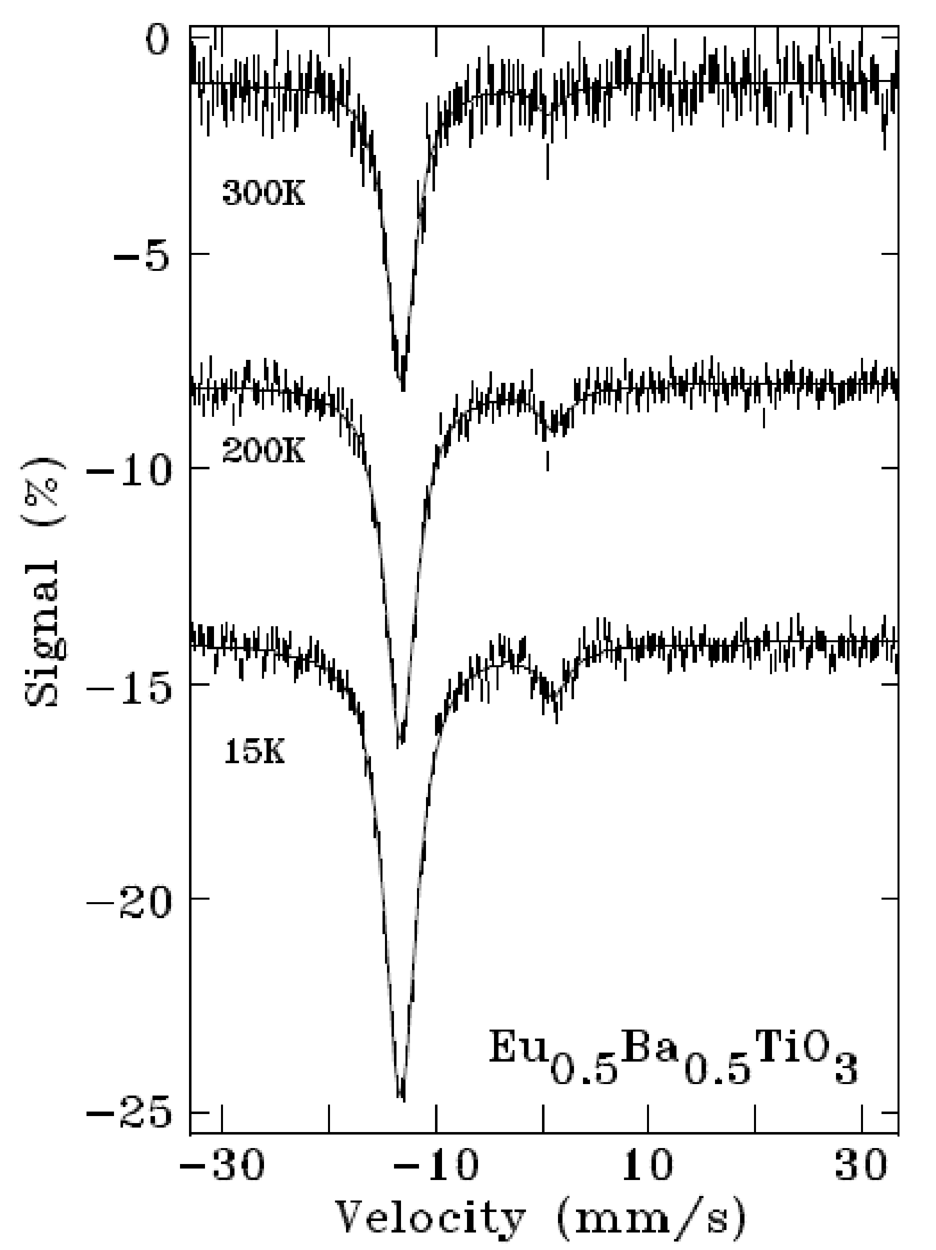
- Isotopic abundance 47.8(5)% Ground state properties:
  μ = 3.4717(6) nm
  Q = 0.903(10) b

- Excited state properties:
  E = 21.541418(10) keV
  E_R = 1.650411(8) 10^{-3} eV
  α_{IC} =28.6(1)
  σ = 3.86(5) 10^{-20}cm^2
  μ = 2.591(2) nm
  Q = 1.28(2) b
  $T_{1/2}$ = 9.6(3) ns
  W = 1.3(3) mm/s
- Production:
  ^{150}Sm(n,γ)^{151}Sm
  ^{151}Eu(p,n)^{151}Gd
  ^{151}Eu(d,2n)^{151}Gd

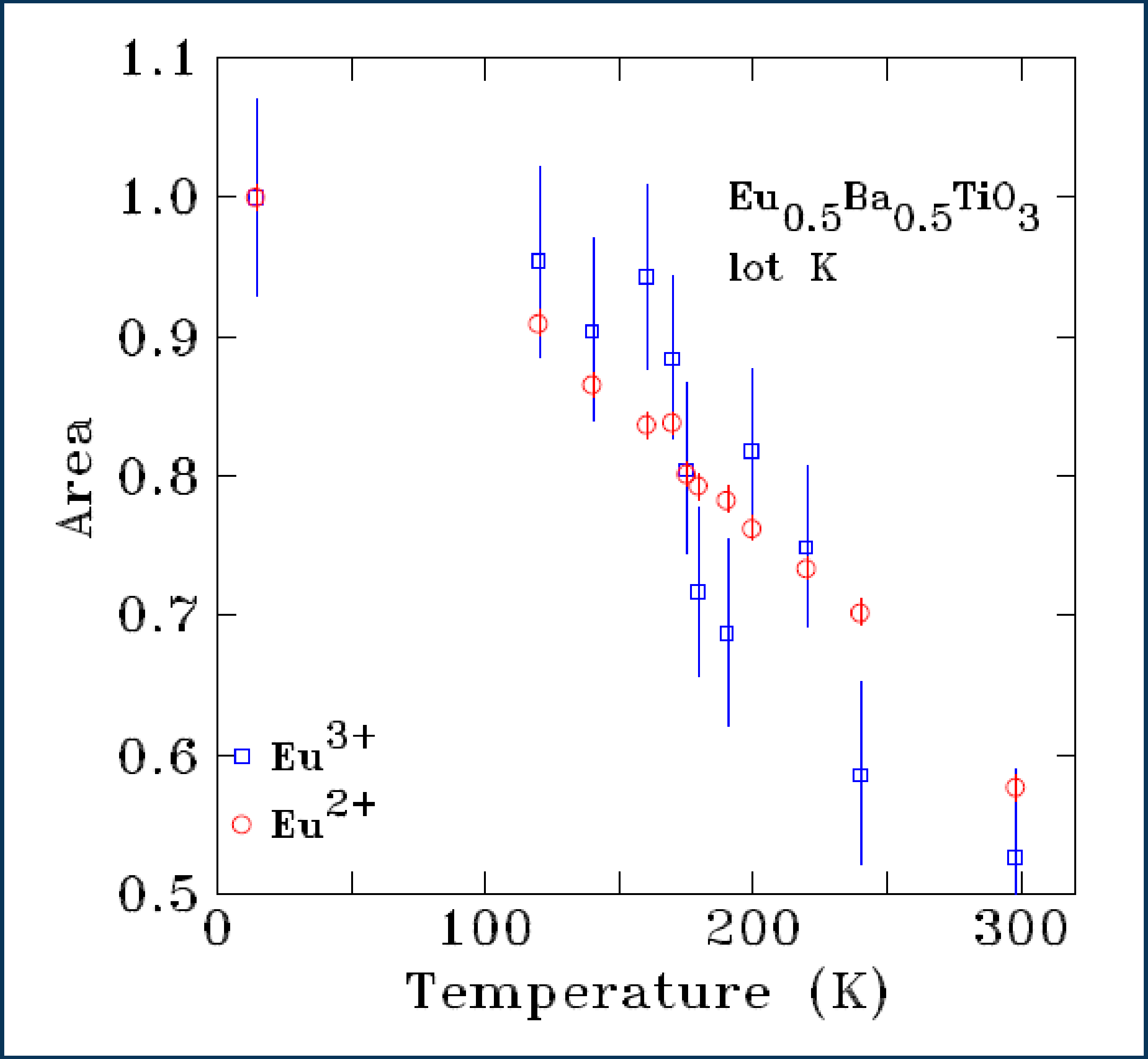


^{151}Eu Mössbauer spectra

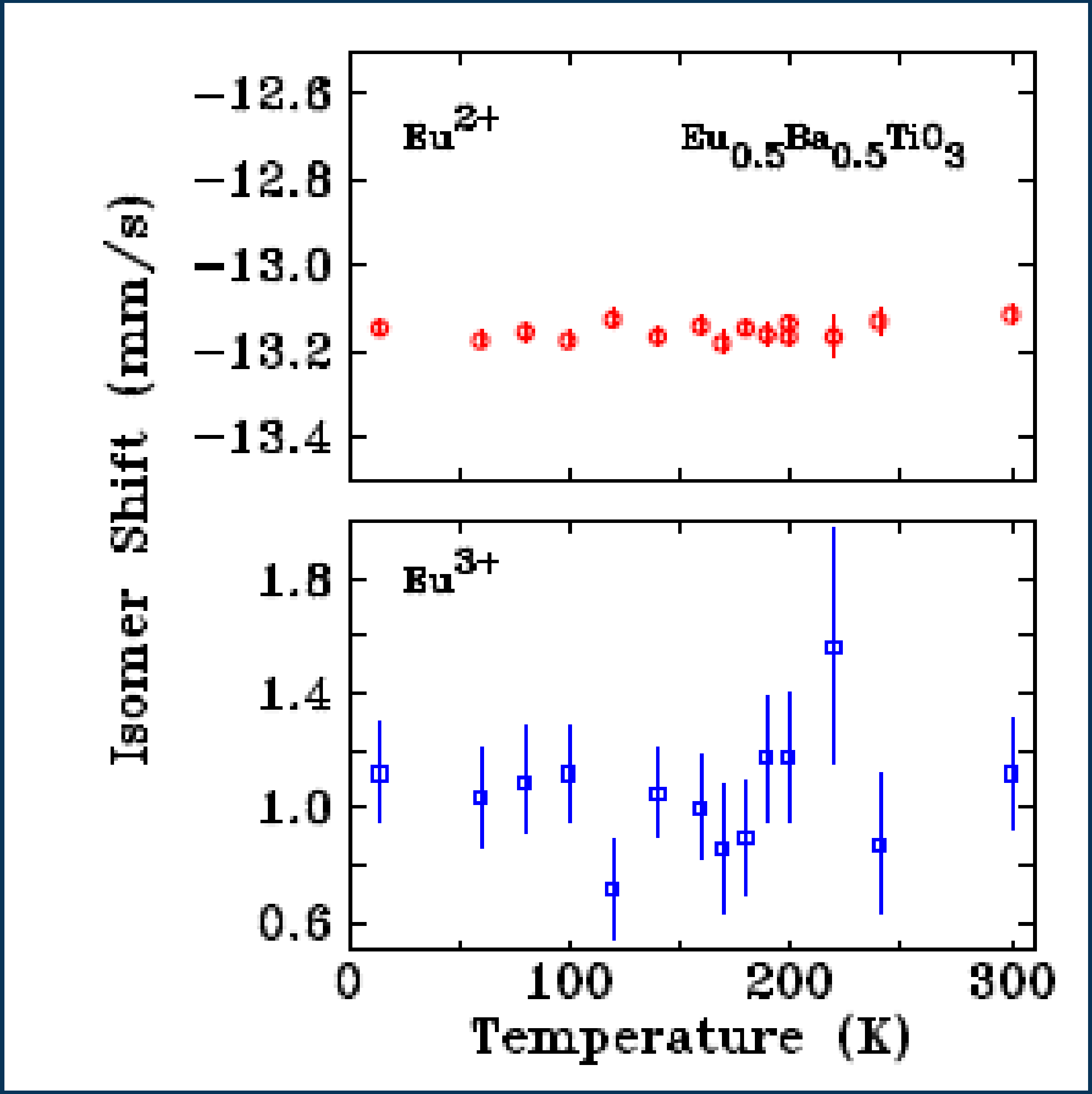
90% 2+
10% 3+   origin ?



Relative Mössbauer areas



Isomer shifts



Eu^{2+}

Eu^{3+}

$Eu_{0.5}Ba_{0.5}TiO_3$

- Why does Eu^{3+} show a much stronger effect than Eu^{2+} ?
- Eu^{3+} is about 15 % smaller than Eu^{2+}
- Why is Eu^{3+} present ? Stoichiometry issues ?

Conclusions

- $Eu_{0.5}Ba_{0.5}TiO_3$ shows a clear effect of the ferroelectric transition at 178 K by ^{151}Eu Mössbauer spectroscopy
- Eu is mainly in the 2+ state but some 3+ is present
- Eu^{3+} shows a much stronger effect than Eu^{2+}.

Thanks

NSERC
CRSNG

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