Francisite: a candidate “antiferroelectric” multiferroic


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CuBi(SeO$_3$)$_2$O$_2$Cl... or simply CBSCI

Iron monarch (open cut mine), Iron Knob, South Australia

Original ore specimen submitted by Glyn Francis in 1987.

Previously unidentified CuBi(SeO$_3$)$_2$O$_2$Cl compound is first characterised in 1990 [A. Pring et al. Am. Mineral. 75: 1421 (1990)].

“...named in recognition of Glyn Francis’ contribution to the understanding and preservation of the minerals of the Iron Monarch ore body.” - A Pring et al. 1990
• **Orthorhombic** *Pmmn* space group (centrosymmetric).  
  [A. Pring *et al.* Am. Mineral 1990]

• CuO$_4$ square plackets produce **buckled Cu$^{2+}$ kagome lattice** layered along *c*.

• Layers are separated by SeO$_3$ triangular pyramids and Bi atoms.

• Cl atoms confined within centres of hexagonal tunnels.
Chapter 6. Weak magnetic excitations in geometrically frustrated CBSCl

Figure 6.1: (a) Crystal structure of room temperature CBSCl (P mmn), with the CuO₄ plackets identified as blue isosurfaces. The hexagonal kagome-like structure is evident in the ab plane (b). The buckled hexagonal lattice due to the different Cu sites appears in the ac plane (c). All graphics generated using VESTA and information in Appendix B.2.

Francisite: CuBi(SeO₃)₂O₂X; X = Cl, Br, I

CuBi(SeO₃)₂O₂Br (CBSBr)
CuBi(SeO₃)₂O₂I (CBSI)

CuY(SeO₃)₂O₂Cl
CuSm(SeO₃)₂O₂Cl
CuEr(SeO₃)₂O₂Cl
Magnetic and dielectric interest

Magnetic frustration/order

Antipolar distortion

Magnetic susceptibility

\[ T_{CW} = +50K \]

\[ T_N = 25K \]

Pcmn

Pmmn

dielectric constant

Millet J. Mater. Chem. 11 (2001)
Antiferroelectrics: real or not?

Theory of Antiferroelectric Crystals
C. Kittel
Department of Physics, University of California, Berkeley, California
(Received January 10, 1951)

Effective field of each sub lattice

\[ F_a = E + \beta_1 P_a - \beta_2 P_b; \quad F_b = E + \beta_1 P_b - \beta_2 P_a. \]

Free energy

\[ A(P_a, P_b, T) = A_0 + f(P_a^2 + P_b^2) + gP_aP_b + h(P_a^4 + P_b^4). \]

Soft-mode spectroscopy: Experimental studies of structural phase transitions*

J. F. Scott
Department of Physics, University of Colorado, Boulder, Colorado 80303
Reviews of Modern Physics, Vol. 46, No. 1, January 1974

"...in general one cannot characterize a crystal at one temperature as antiferroelectric by any set of experimental measurements at that temperature."

"...antiferroelectricity is an ill defined, almost useless concept."

\[ P_{\text{total}} = 0 \]

How do you define a sub lattice polarisation?

No macroscopic order parameter

No broken symmetries!

Sawaguchi Phys. Rev. 83 (1951)

Soft mode.

Sawaguchi Phys. Rev. 83 (1951)

Sawaguchi Phys. Rev. 83 (1951)

Sawaguchi Phys. Rev. 83 (1951)

\[ \phi(\eta, P, T) = \phi_0(T) + \frac{\alpha}{2} \eta^2 + \frac{\beta}{4} \eta^4 + \frac{\gamma}{6} \eta^6 + \frac{P^2}{2} \chi_0 \]

- local polar point group symmetry as order parameter.
- Displacive AFE characterised by soft antipolar phonon mode
Antiferroelectric signatures

- Antipolar atomic displacements
- Phase transition between two non-polar phases
- Dielectric anomaly at the transition
- Polar phase induced by electric field

**Uses**
- Energy storage
- Electrocalorics
- Large strain actuators
- (Multistate) memories

**Issues**
- Ambiguities of the double loop.
- What is a sublattice polarisation?
- Absence of a symmetry criterion.
- Antiferroelectricity in PbZrO3 is a complex model.
Lattice contribution to dielectric response along $a$

Antipolar distortion

$P_{cmn}$  

$P_{mmn}$

$T_c = 115$ K

Teamperture (K)

Dielectric constant

$\varepsilon(0) \propto T^3$

Far-infrared reflectivity

$\varepsilon$ vs. Frequency (cm$^{-1}$)

Complex transmission

THz spectroscopy

PPMS (1 kHz $E \parallel a$)
Lattice contribution to dielectric response along a

Kramers-Kronig transform

- E || a
- E I a
- P0
- P1
- P2

Frequency (cm$^{-1}$)

Temperature (K)

- $T_N$
- $T_c$

FWHM (cm$^{-1}$)
Lattice contribution to dielectric response along $a$

Dielectric response over a range of temperatures and frequencies is shown. The graphs depict the dielectric constant as a function of frequency and temperature. Peaks labeled P0, P1, and P2 indicate specific vibrational modes, with the dielectric constant showing a peak at higher temperatures.

Temperature and frequency scales are marked on the x- and y-axes, respectively. The dielectric constant $\varepsilon(0)$ is plotted against temperature, with different extrapolation methods indicated (KK reflectivity and PPMS).
Dielectric response of soft antipolar mode

![Graph showing frequency and FWHM vs. temperature](image)

- Frequency (cm$^{-1}$)
- FWHM (cm$^{-1}$)
- Temperature (K)

Arrows indicating cooling direction.
Dielectric response of soft antipolar mode

![Graph showing frequency and FWHM vs. temperature](image_url)
Dielectric response of soft antipolar mode

![Graph showing dielectric response with frequency and FWHM vs. temperature.](image)

- Frequency (cm\(^{-1}\)) vs. Temperature (K)
- FWHM (cm\(^{-1}\)) vs. Temperature (K)

**Unit cell doubling**
Dielectric response of soft antipolar mode

- Frequency (cm⁻¹)
- FWHM (cm⁻¹)
- Temperature (K)

- Cooling
- Raman active zone
- Centre mode
- Mode repulsion
Raman phonon dynamics
Inelastic xray scattering soft mode dispersion

Z point (5 0 0.5)

300 K

THz spec
Inelastic X-ray scattering soft mode dynamics
Elastic Thermal Diffuse X-ray Scattering (TDS)

Soft-mode frequency
Elastic Thermal Diffuse Xray Scattering (TDS)
Antipolar softmode dynamics

\[ G(\eta) = A(T-T_c)\eta^2 + B\eta^4 \]

Slope ratio: 3.4
Antipolar softmode dynamics

Magnetic correlations: $J_1 = 76$ K
**Two S = 1/2 Cu$^{2+}$ sites:** Cu1 at (0,0,0) 4c and Cu2 at (1/4, 1/4, z) 2c.

\[
H = J_1 \sum_{i=1,3} S_i \cdot S_j + J'_1 \sum_{i=1-4 \atop j=5} S_i \cdot S_j + J_2 \sum_{i=1,2 \atop j=3,4} S_i \cdot S_j \\
+ J_{\perp 1} \sum_{i=1-4 \atop j=6} S_i \cdot S_j + J_{\perp 2} \sum_{i=5 \atop j=6} S_i \cdot S_j + D \cdot \sum_{i=1-4 \atop j=5} S_i \times S_j,
\]

Magnetic structure: $k = (0, 0, 1/2)$ antiferromagnet
S = 1/2 antiferromagnetic kagome lattice is the archetype of quantum spin liquids.

Francisite represents **kagome system beyond nearest neighbour antiferromagnets:**

- Nearest neighbour ferromagnetic interactions.
- Competing antiferromagnetic interactions across hexagonal voids.

**May support novel phases:**

- Non-coplanar spin correlation and spin liquid states  
  - e.g. Kapellasite [B. Fåk PRL 2012]
- Magnetically induced ferroelectricity:
  - e.g. multiferroic KCi$_3$As$_2$O$_7$(OD)$_3$ [G. L. Nilsen PRB(R) 2014]
Q = (0 k 2) map comparison with simulation

- Dispersion shape and extinction along k reproduced well in simulations using proposed Hamiltonian.
- No dispersion along l confirms very weak interlayer coupling and “global” spin gap.
- Simulation does not reproduce spin gap.
A spin gap is induced by incorporating an anisotropic exchange between Cu1 sites along $y$.

Modification of $J_2$ produces correct canting of Cu2 spins as refined by neutron diffraction.

\[ H = J_1 \sum_{i=1,3, j=2,4} S_i \cdot S_j + J'_1 \sum_{i=1,5} S_i \cdot S_j + J_2 \sum_{i=3,4} S_i \cdot S_j + J_{\perp 1} \sum_{i=1,4} S_i \cdot S_j + J_{\perp 2} \sum_{i=5} S_i \cdot S_j + D \sum_{i=1,4} S_i \times S_j + S_i \cdot \Gamma_{i,j} \cdot S_j, \]

\[ J_1 = -6.55 \text{ meV} \quad J'_1 = -5.75 \text{ meV} \]
\[ J_{\perp 1} = 0.035 \text{ meV} \quad J_{\perp 2} = 0.17 \text{ meV} \]
\[ J_2 = 4.9 \text{ meV} \quad D_x = 1.04 \text{ meV} \]

\[ \Gamma_{5,2} = \begin{pmatrix} 0.10 & 0.08 & 0.00 \\ 0.08 & 0.00 & 0.04 \\ 0.00 & 0.04 & 0.00 \end{pmatrix}, \quad \Gamma_{1,2} = \begin{pmatrix} 0.00 & 0.00 & 0.00 \\ 0.00 & 0.05 & 0.12 \\ 0.00 & 0.12 & 0.05 \end{pmatrix}, \quad \Gamma_{4,2} = \begin{pmatrix} -0.7 & 0.0 & 0.0 \\ 0.0 & 0.0 & 0.0 \\ 0.0 & 0.0 & -1.7 \end{pmatrix}. \]

[Rousouchatzakis et al. PRB (2015)]
Overlapping magnon / phonon bands

- Overlapping magnon and phonon bands: Possibility for magnon phonon hybridisation.
- Spin-lattice coupling could promote the required anisotropy in the refined magnetic Hamiltonian.
- Polarised inelastic neutron scattering required to reveal signatures of such hybridisation.
Soft phonon dynamics in \textbf{b} direction

- Reflectance vs. Frequency for different temperatures (10 K, 120 K, 300 K).
- \( \varepsilon_1 \) and \( \varepsilon_2 \) shifts for different temperatures.
- Peak Amplitude vs. Temperature for different peak frequencies (P0, P1, P2).
- FWHM vs. Temperature for different peak frequencies.
Soft phonon dynamics in \textbf{b} direction

Reflectance

Frequency (cm\(^{-1}\))

Peak Frequency (cm\(^{-1}\))

Peak Amplitude

Energy transfer (meV)

FWHM (cm\(^{-1}\))

Temperature (K)

\(Q = (0,k,2)\)
Spontaneous polarisation along $c$ for $T < T_N$

- magnetic point group: $mm'm$ supports magneto electric coupling but **does not predict spontaneous polarisation at 0 T**.

- Field dependence is consistent with the off diagonal terms in the ME tensor.

- Presence at 0 T could be explained by magneto electric coupling due to stray fields generated at defects.

- Effect of antiferrroelectric order?

\[
\alpha^{ME}_{ij} = \begin{pmatrix}
    0 & 0 & \alpha^{ME}_{13} \\
    0 & 0 & 0 \\
    \alpha^{ME}_{31} & 0 & 0
\end{pmatrix}
\]

maximised with $HxE$
Concluding remarks

- Francisite displays a **novel frustrated magnetic** state:
  - Buckled kagome lattice with nn FM and nnn AFM interactions.
  - Touching soft magnon bands, dispersionless along $l$ (quasi 2-D).
  - Spin gap requiring anisotropic exchange modification to Hamiltonian.
  - Supports spontaneous polarisation below $TN = 25 K$.

- Identification of $Pmmn \rightarrow Pcmn$ transition driven by **antipolar soft mode**:
  - candidate displacive “antiferroelectric”
  - Evidence of spin-lattice coupling.
  - Significance of magnetic/antiferroelectric order in domain of multiferroics?

- Still much of the phase space to be explored with many possible substitutions in the chemical formula.