

Computational Studies of Magnetically Frustrated $M'M''_3Si_2Sn_7O_{16}$ ($M' = Fe, Co; M'' = Fe, Mn$) Structures.

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01: Initial Observations (Credit: T.Söhnel, C. Ling, M. Allison)

$Fe_4Si_2Sn_7O_{16}$

Low temperature Neutron Powder Diffraction studies¹ of the bi-layered $Fe_4Si_2Sn_7O_{16}$ (Fig.1) revealed a magnetically frustrated Kagomé lattice in its oxide layer, below $T_N = \sim 3K$.

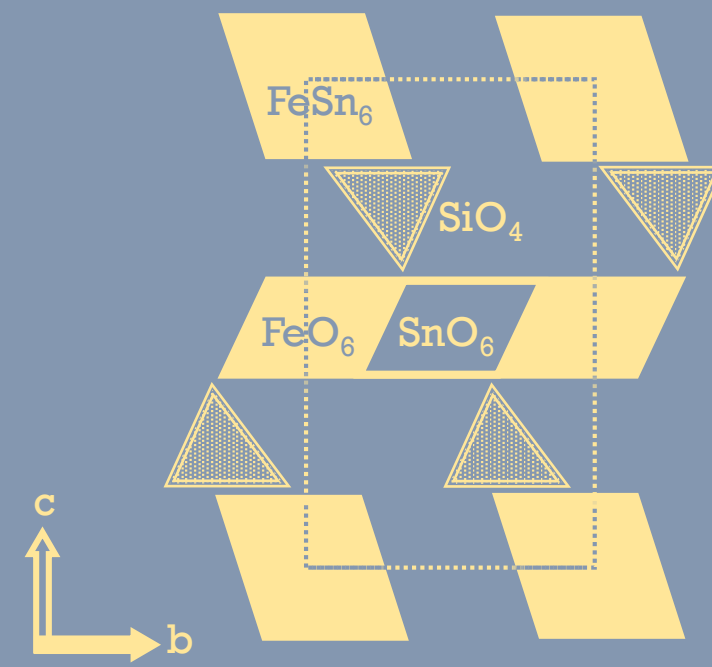


Figure 1. Bi-layered $Fe_4Si_2Sn_7O_{16}$ Crystal Structure

Broken Symmetry

This forms a magnetic supercell: Fe sites along canted anti-ferromagnetic chains (Fig.2) are AFM with respect to sites along y & xy , as well as along z (propagation vector of $(0, \frac{1}{2}, \frac{1}{2})$)

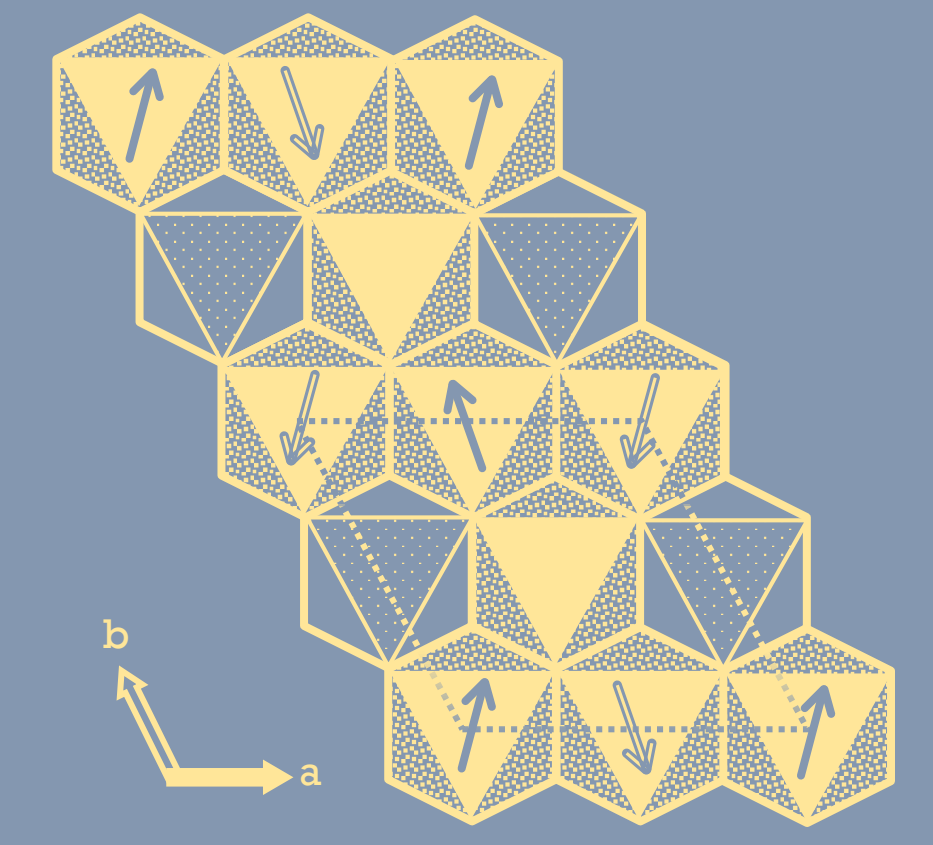


Figure 2. Magnetic Kagomé lattice made up of Fe sites in the $Fe_4Si_2Sn_7O_{16}$ oxide layer.

02: Magnetic Structure - Theory

Frustration

Frustrated AFM structures arise from competing exchange interactions²; the most simple example shown in Figure 3, where the direct AFM nearest-neighbour exchange (J_1) cannot be satisfied between all three atoms, leaving one magnetically frustrated.

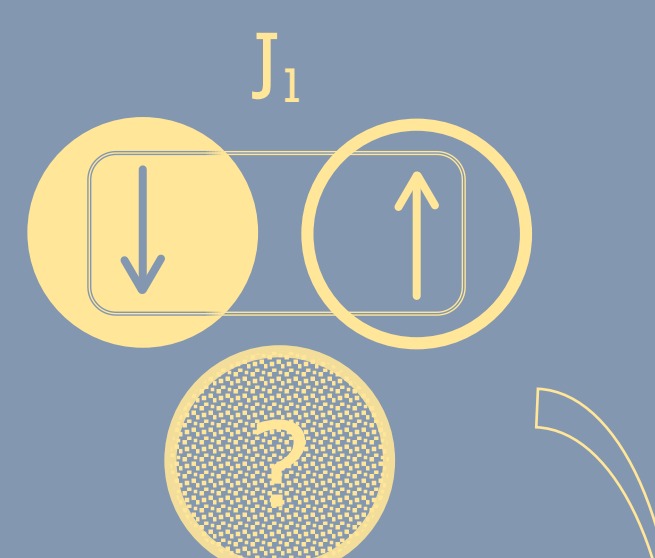


Figure 3. Idealised AFM magnetic frustration

We see the same concept in our structure (Fig.4): the dominant J_1 direct exchange cannot be satisfied within the hexagonally ordered Fe sites, resulting in a frustrated 'inter-chain' site. Why, though, do the chains propagate along x , instead of the symmetrical y and xy directions?

Additional Pathways

A next-nearest-neighbor AFM exchange also exists between the chains, along both y and xy (J_d). These distances are outside the range of direct exchange, however, superexchange interactions mediated by intermediate anions (Oxygen in this instance) could play a role.

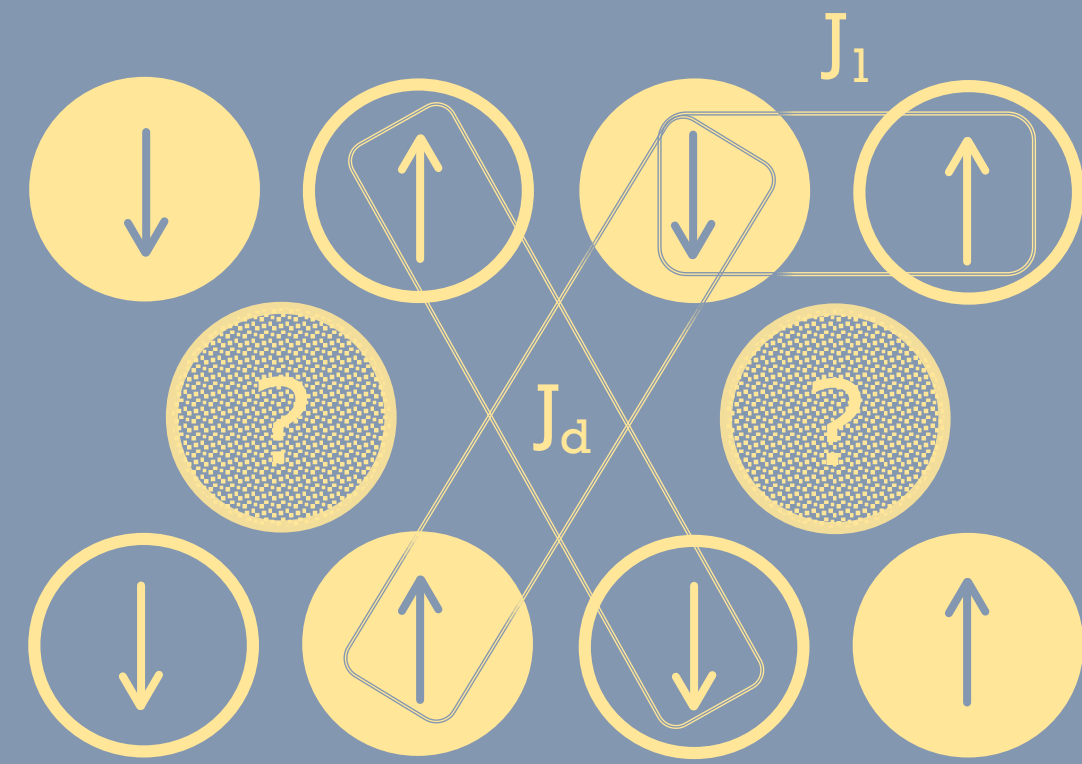


Figure 4. AFM frustration as present in the $Fe_4Si_2Sn_7O_{16}$ oxide layer, with magnetic exchange interactions indicated.

Super-Superexchange

Typical superexchange interactions occur through an intermediate anion, with occupancy of metal d-orbitals and the Metal-Anion-Metal angle determining the type of interaction (FM/AFM)³.

For this structure we see a potential 'super-superexchange' with two intermediate anions (Fig.5). Anion-anion distance was found to be a significant factor in the strength of such a pathway⁴ and for $Fe_4Si_2Sn_7O_{16}$ we see that the shortest anion-anion distance is along the edges of SnO_6 octahedra (Fig.5).

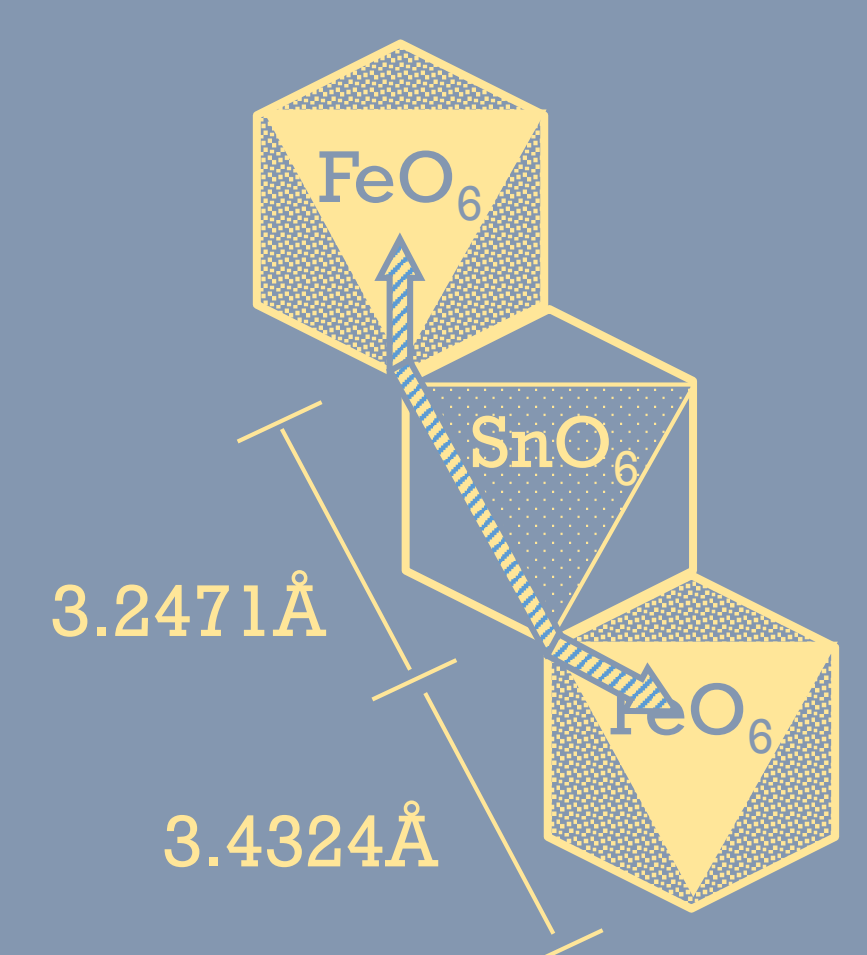


Figure 5. Anion-anion distances present in the $Fe_4Si_2Sn_7O_{16}$ oxide layer; with proposed Fe-O-O-Fe pathway indicated by arrow-line

This still does not answer the question of preferential AFM chain propagation, for that we need to move to computational methods.

03: Magnetic Structure - Computation

Bonding Analysis

COHP bonding analysis was performed using LOBSTER⁵ to look at orbital interactions; while we may not be looking at bonding interactions, we are still interested in what COHP analysis can tell us about spatial overlap and symmetry relationships, as these elements are also important for the weaker magnetic exchange interactions³.

COHP analysis reveals greater orbital interactions on the edges of SnO_6 octahedra, in agreement with the shorter O-O distance compared to FeO_6 . Furthermore, these interactions aren't isotropic with respect to the xy plane, with a more significant overlap occurring between $O_{2py}-O_{2py}$ along y (Fig. 6a).

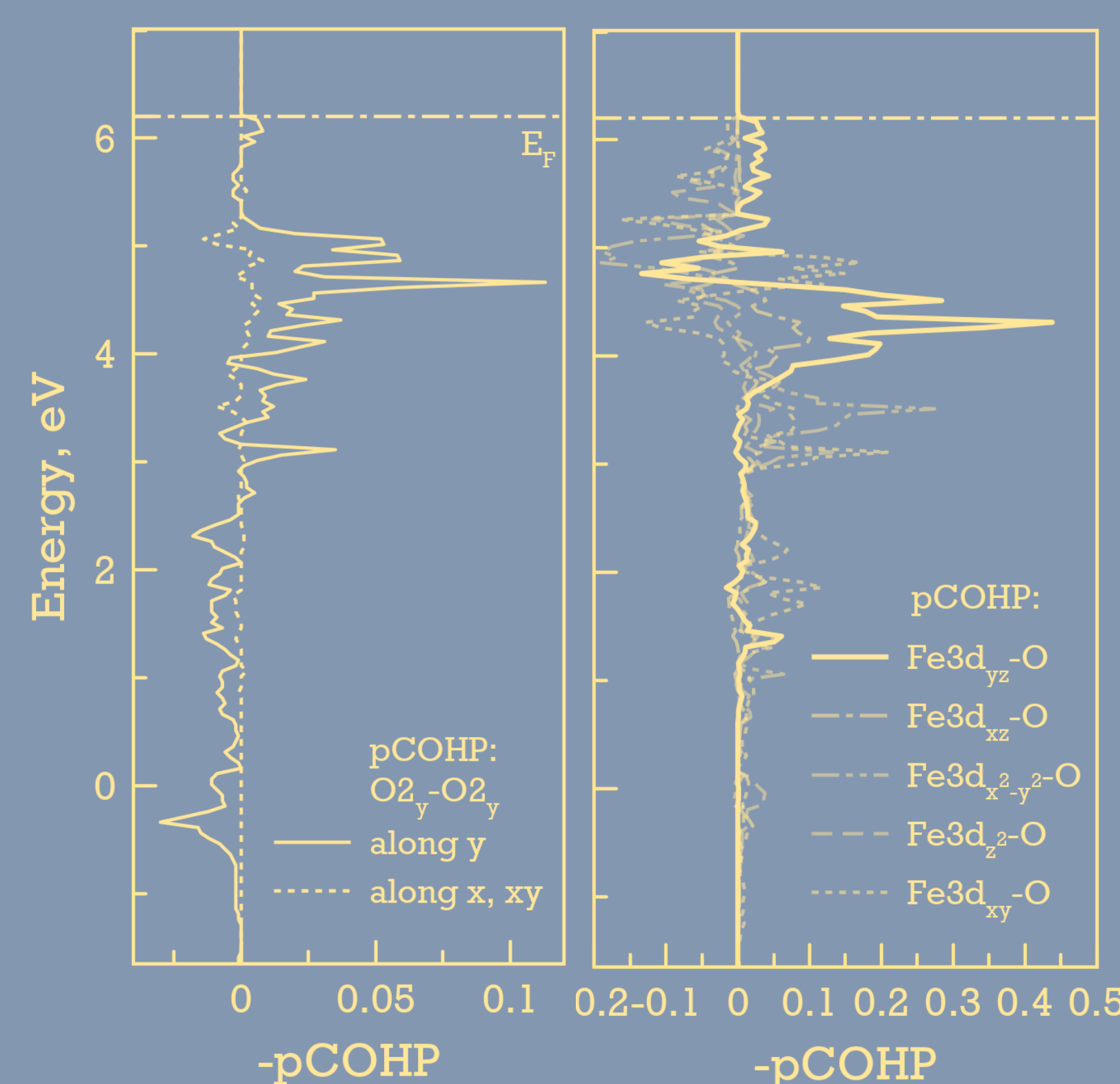


Figure 6. a) Direction dependant O-O orbital overlap along SSE pathways. b) Overlap of Fe-3d orbitals with Oxygens shown in 6(a).

COHP analysis of Fe 3d orbitals (Fig.6b) shows the most significant overlap occurring between $Fe-3d_{yz}$ and the above-mentioned Sn bound O sites (along y). Following a similar SSE mechanism as in $LiCuVO_4$ ⁶, the pathway responsible for J_d is proposed to be: $Fe3d_{yz}-O2p_y--O2p_y-Fe3d_{yz}$ (Fig. 7).

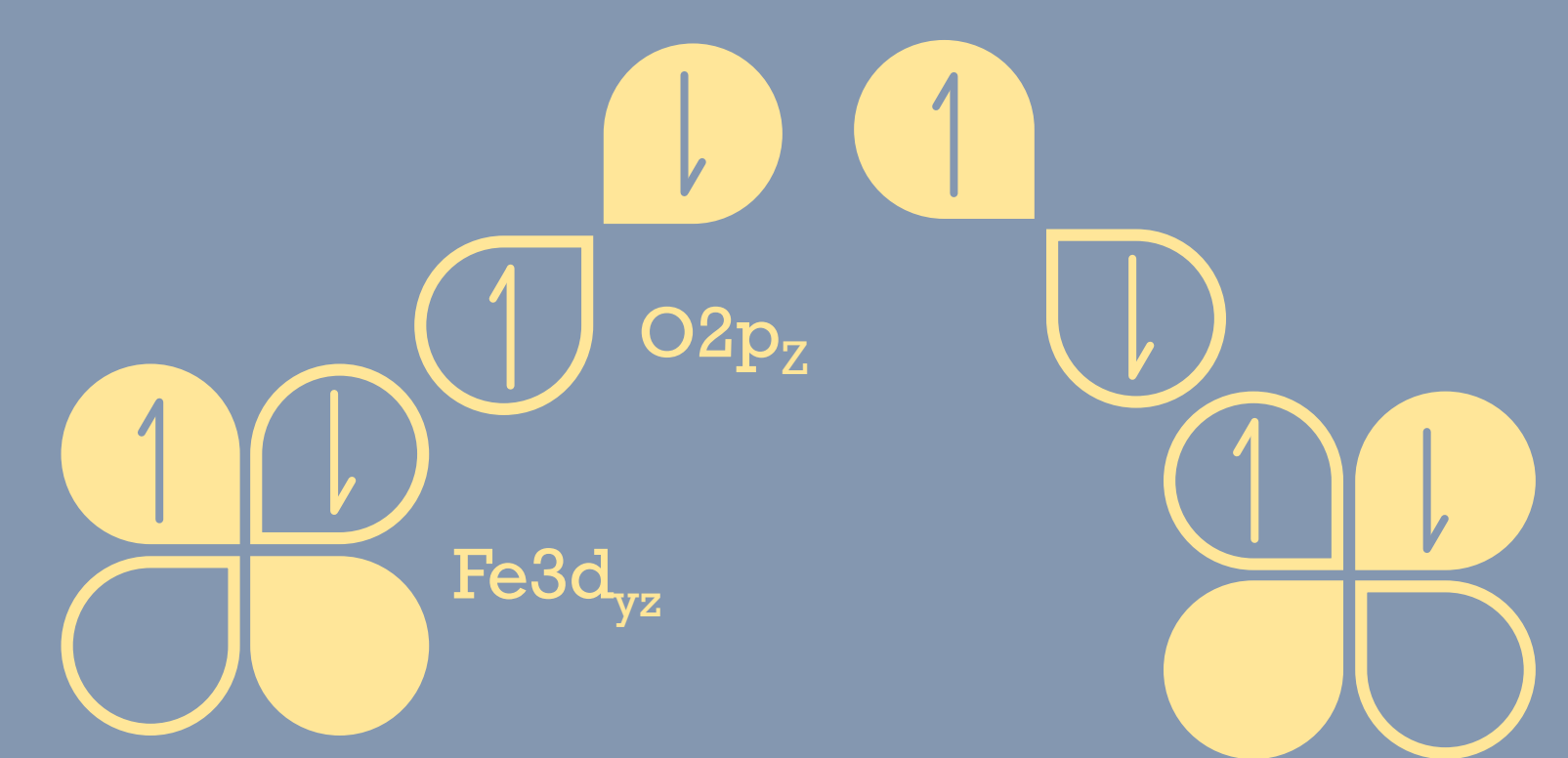


Figure 7. Proposed SSE pathway along y

04: Interlayer exchange

If we attempt to build a similar super-superexchange pathway to account for the longer distance 'interlayer' AFM exchange ($+/-1c$), we are able to trace an Fe-O-O-Fe pathway (Fig.8). Unlike the proposed J_d pathway, this does not involve direct Fe-O bonds. The Oxygen sites in question, however, are part of bridging SiO_4 tetrahedra and are bound to two Sn, resulting in a distorted trigonal planar (sp^2) arrangement. This leaves an electron lone pair in the remaining p orbital, which just so happens to be oriented toward the $Fe-3d_{z^2}$ orbital. Furthermore, the O-O distance is only ~ 0.15 Angstrom larger than the J_d pathway which, as stated, is a critical factor in such a pathway.

An accounting of dominant exchange interactions can now be proposed. In descending order of exchange energy we have: a direct AFM exchange along x (J_1), a SSE along y (J_d) and a SSE along z . Quantifying these exchange energies through computational methods, along with observing the effect of systematic substitutions on the magnetic structure, such as increasing the interlayer distance and hence weakening the interlayer TM-O-O-TM pathway, would help to confirm what has been proposed above.

05: References & Affiliations

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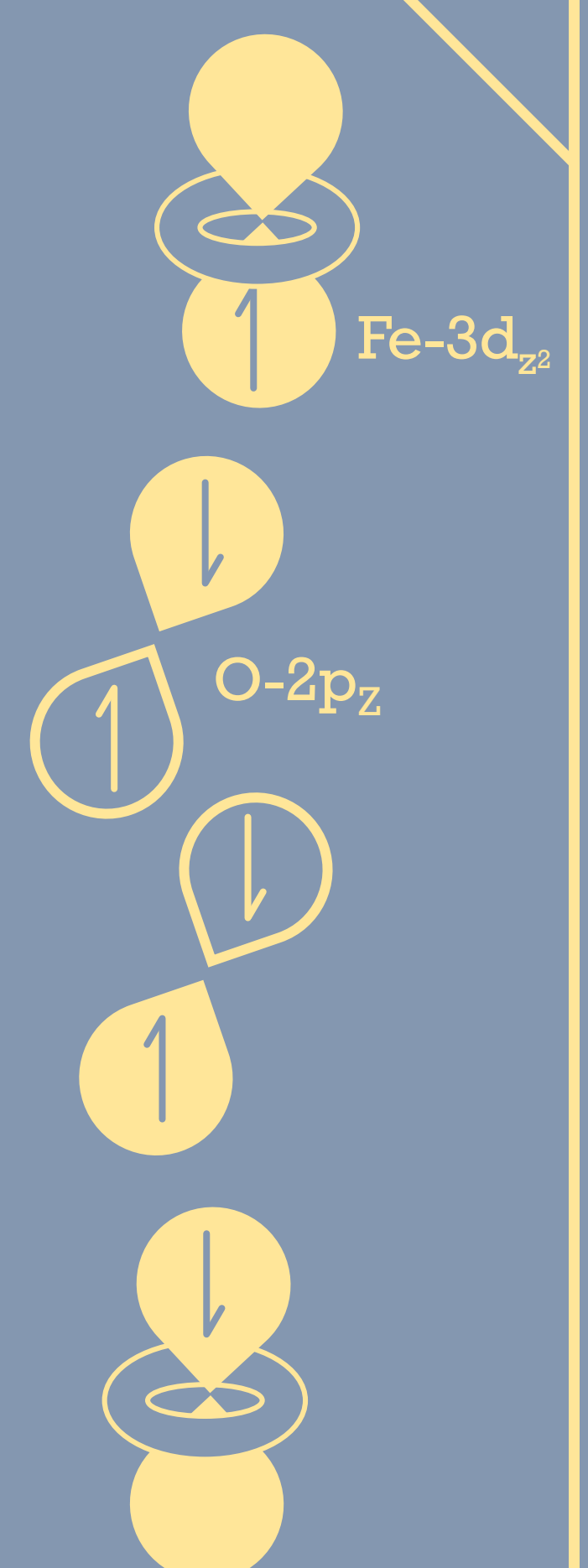


Figure 7. Proposed 'interlayer' SSE Pathway.