

**PbFePO₄F₂ with a 1/6th bond depleted Triangular Lattice**

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PbFePO₄F₂ with a 1/6th bond depleted Triangular Lattice

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We hydrothermally synthesized a layered PbFePO₄F₂ (P2₁/n). Fe³⁺ cations ($S = 5/2$) within the layer are connected via F⁻ and (PO₄)³⁻ anions to give a novel (distorted) 1/6th bond depleted triangular lattice. The $\chi(T)$ suggests strong antiferromagnetic interactions with Weiss constant of -125 K, but geometrical frustration and low dimensionality appears to prohibit a long-range order down to 23 K.

Mixed-anion compounds have been a topic of extensive research owing to novel functional properties,¹ including non-toxic pigments (e.g. LaTaON₂),² visible-light-responsive photocatalysts (e.g. Bi₄NbO₈Cl),³ nonlinear optical materials (e.g. C₁₀H₁₀N₃NbOF₄),⁴ and electrodes (e.g. AgNa(VO₂F₂)₂).⁵ Inclusion of anion-groups (polyanion) such as (BO₃)³⁻, (CO₃)²⁻ and (PO₄)³⁻ further enriches chemical bonds and thus available functionalities. Fluorides combined with anion groups are particularly promising as nonlinear optical materials because of the ability of the fluorine ion to blue-shift the absorption edge, such as KBe₂BO₃F₂⁶ and NH₄B₄O₆F⁷ with (BO₃)³⁻ and Ba₂VO₂(IO₃)₃F₂⁸ with (IO₃)⁻. Besides, when non-d⁰ transition metal is used, various magnetic lattices with tuneable exchange interactions result.⁹⁻¹²

Geometrically frustrated spin systems are known to exhibit exotic phenomena such as successive phase transitions, non-trivial spin textures and spin liquid state.¹³⁻¹⁵ The triangular lattice (Figure 1a) is an archetypal system that has been examined since the earliest days of research in frustrated magnetism.¹⁶ Later, the attention has shifted to kagomé lattice (Figure 1b), a 1/4th site depleted triangular lattice ($d = 1/4$) since the reduced coordination number of $z = 4$ (vs. 6) could enhance quantum fluctuations.¹⁷ The honeycomb lattice with a 1/3th site depletion ($d = 1/3$, $z = 3$), shown in Figure 1c, can be frustrated when the next-nearest-neighbour is added,¹⁸ and

also represents the exactly solvable Kitaev model.¹⁹ Although much less investigated, other site depleted triangular lattice derivatives are reported, such as 1/4th and 1/6th site depleted triangular lattices (Figure 1d and e) in K₂Mn₃(VO₄)₂(OH)₂^{20, 21} and Mn₅(VO₄)₂(OH)₄,²¹⁻²³ and a maple-leaf lattice (Figure 1f) in MgMn₃O₇·3H₂O.²⁴ Besides site depletion, bond depletion could also obtain triangular lattice derivatives,²⁵ such as cube tile lattice with 1/3th bond depletion (Figure 1g) as found in CsFe₃(SeO₃)₂F₆.²⁶

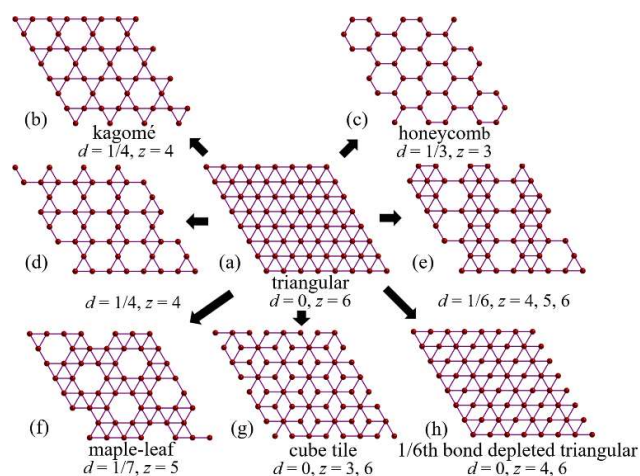


Fig. 1 Evolutions of triangular lattice: (a) triangular lattice,¹⁶ (b) kagomé lattice,¹⁷ (c) honeycomb lattice,^{18, 19} (d) 1/4th site depleted triangular lattice,^{20, 21} (e) 1/6th site depleted triangular lattice,²¹⁻²³ (f) maple-leaf lattice,²⁴ (g) cube tile lattice,²⁶ (h) 1/6th bond depleted triangular lattice (this work), where d is the number of site depletion from triangular lattice and z is the coordination number.

When one alternately removes bonds along one direction, one obtains a lattice with $d = 0$ and $z = 4$ and 6, which we call hereafter a 1/6th bond depleted triangular lattice (Figure 1h). In this study, we have hydrothermally synthesized an iron phosphate fluoride containing (PO₄)³⁻ anions, PbFePO₄F₂. The consideration of exchange pathways suggests that PbFePO₄F₂ is an experimental realization of the distorted 1/6th bond

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depleted triangular lattice. Magnetic measurement indicates a sizable spin frustration and low dimensionality.

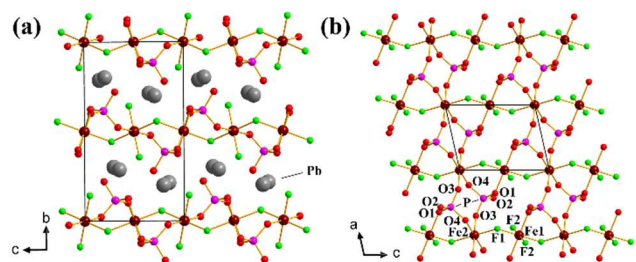


Fig. 2 Crystal structure of PbFePO₄F₂ viewed along (a) [100] and (b) [010].

PbFePO₄F₂ was hydrothermally synthesized by using 0.2 g Pb₃O₄, 0.1 g FeO, 0.4 mL H₃PO₄, 0.8 mL 48% aqueous HF (*caution!*). Experimental details for synthesis and characterization are described in Supporting Information. Single crystal X-ray diffraction has revealed that this compound crystallizes in a layer structure with the space group *P2₁/n*. The PXRD is shown in Figure S1. The unit cell parameters are *a* = 5.257(2) Å, *b* = 12.404(5) Å, *c* = 7.098(3) Å and β = 102.8(1)° (*Z* = 4). There are two Fe atoms, one Pb atoms, one P atom, two F atoms, four O atoms in its asymmetric unit. As shown in Figure 2, (Fe₂PO₄)²⁻ layers, separated by 12-coordinated Pb²⁺ cations, stack along [010] with a distance of 6.202(3) Å (half of the *b* axis). In the Fe₂PO₄ layer, two iron-centered heteroleptic octahedra, Fe(1)O₂F₄ and Fe(2)O₄F₂, are alternately connected through the F⁻ and (PO₄)³⁻ ligands to form the doubly-bridged Fe(1)–F(1)/(PO₄)–Fe(2) chains along [001] (Figure 2b). This provides the shortest Fe–Fe distance of 3.5490(15) Å. These chains are linked by the (PO₄)³⁻ groups within the *ab* plane. The Fe(1)O₂F₄ octahedron has fluorine anions at the equatorial sites (*d*_{Fe(1)–F(1)}} = 1.941(5) Å × 2 and *d*_{Fe(1)–F(2)}} = 1.933(5) Å × 2) and oxide anions at the apical site (*d*_{Fe(1)–O(1)}} = 1.985(5) Å × 2). The Fe(2)O₄F₂ octahedron has equatorial O²⁻ anions (*d*_{Fe(2)–O(3)}} = 1.978(5) Å × 2, *d*_{Fe(2)–O(4)}} = 2.074(5) Å × 2) and apical F⁻ anions (*d*_{Fe(2)–F(1)}} = 2.012(5) Å × 2). The P–O bond length in the PO₄ group ranges from 1.518 Å to 1.552 Å, which agree with those reported.⁹ Other bond lengths and angles are summarized in Table S2. The oxidation states of +3 in iron (calculated values: 3.03 for Fe(1) and 2.76 for Fe(2)), +5 in phosphorus (calculated value: 4.83) are confirmed by bond valence sum (BVS) calculations using values reported by Brese and O’Keefe (see Table S2).²⁷ Upon heating, a powder sample starts to decompose around 200 °C (Figure S3) and the final product after TGA is identified as Pb₃Fe(PO₄)₃ and hematite Fe₂O₃ (Figure S1). The weight loss of 6.2% is in good agreement with the calculated loss of 5.6%.

The temperature dependence of the magnetic susceptibility measured at 0.1 T is shown in Figure 3a. A Curie-Weiss fitting was conducted in a high temperature range between 150 K and 350 K, giving an effective magnetic moment of *P*_{eff} = 5.96(1) μ_B and a Weiss constant θ = –125.6(6) K. The *P*_{eff} value is fairly consistent with the theoretical value of 5.92 μ_B for *S* = 5/2. The value of θ indicates predominant antiferromagnetic interactions. As the temperature decreases, the magnetic susceptibility shows a kink around 23 K, suggesting the onset of an antiferromagnetic ordering. A slight upturn of χ(*T*) below 17

K is ascribed to a small amount of defects, referred as Curie tail;^{28, 29} a fitting yielded 0.63% of free *S* = 5/2 spins (Figure S4a). When measured at 6 T, the kink position slightly shifts to a lower temperature of 21 K (Figure S4b). The isothermal magnetization at 2 K (and 300 K) linearly increases with the moment of 0.33 μ_B at 7 T (Figure 3b), in agreement with the antiferromagnetic ground state.

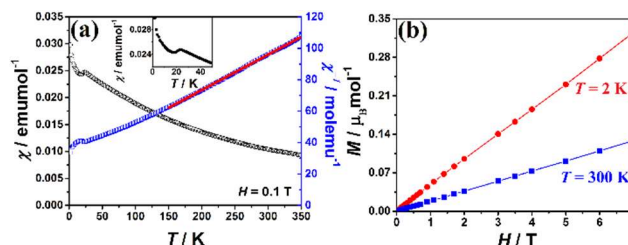


Fig. 3 (a) Magnetic susceptibility χ(*T*) (black) and its inverse χ(*T*)⁻¹ (blue) for PbFePO₄F₂ at 0.1 T, the inset is magnified χ(*T*) around *T*_N. (b) Magnetization *M*(*H*) for PbFePO₄F₂ at 300 K (blue) and 2 K (red).

Let us discuss the magnetic interactions in PbFePO₄F₂ from the viewpoint of the crystal structure. As mentioned earlier, Fe(1) and Fe(2) are connected via F⁻ and (PO₄)³⁻ anions along [001] (Figure 2b). Given the Fe(1)–F(1)–Fe(2) bridging angle of 127.7°, this pathway would provide, according to Goodenough-Kanamori rule,^{30, 31} strong antiferromagnetic superexchange interactions *J*₁ (see Figure 4 and S5a). These Fe chains are linked by (PO₄)³⁻ groups within the *ac* plane, giving super-superexchange interactions. Here, Fe(2) cations in the neighboring chains (*d*_{Fe(2)–Fe(2)}} = 5.257(2) Å) are doubly-bridged by two PO₄ groups to give *J*₂, while Fe(1) is connected to Fe(2) (*d*_{Fe(1)–Fe(2)}} = 5.657(18) Å) via a single PO₄ group to give *J*₂′ (Figure 4 and S5a). There is no magnetic exchange pathway between two Fe(1) cations despite a similar distance of *d*_{Fe(1)–Fe(1)}} = 5.257(2) Å. The interlayer interactions should be much smaller since the Fe₂PO₄ layers are separated by Pb cations.

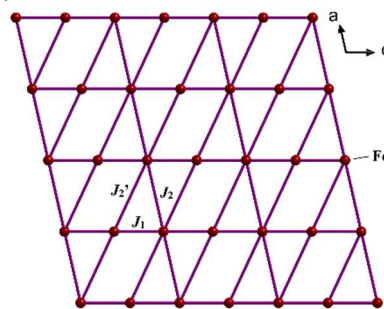


Fig. 4 A distorted 1/6th bond depleted triangular lattice in PbFePO₄F₂.

As a result, the magnetism of PbFePO₄F₂ can be described by a ‘distorted’ 1/6th bond depleted triangular lattice with *J*₁, *J*₂ and *J*₂′, as shown in Figure 4. A degree of frustration is typically estimated using the frustration index *f*, which is defined by *f* = |θ|/*T*_N. For PbFePO₄F₂, *f* is calculated as |θ|/*T*_N = |–125.6|/23 = 5.5, suggesting moderate frustration.^{13, 15, 32} In the absence of further magnetic measurements such as elastic/inelastic neutron scattering as well as DFT calculations, the sign and magnitude of *J*₂ and *J*₂′ remains unclear. However, the magnetic superexchange interaction mediated by PO₄ groups could be strong and significantly important, as manifested in VODPO₄·0.5D₂O³³ and (VO)₂P₂O₇^{34–36} by inelastic neutron scattering, electron spin resonance (ESR) and nuclear magnetic

resonance (NMR) measurements. Thus, in $\text{PbFePO}_4\text{F}_2$ J_2 and J_2' could be comparable in the magnitude with J_1 . We believe that the present study will stimulate theoretical investigations of the 1/6th and other bond depleted triangular lattices.

Conclusions

An iron phosphate fluoride $\text{PbFePO}_4\text{F}_2$ has been hydrothermally synthesized and structurally characterized by single crystal X-ray diffraction. $\text{PbFePO}_4\text{F}_2$ is an experimental correspondence of a 'distorted' 1/6th bond depleted triangular lattice. Despite strong antiferromagnetic interactions with $\theta = -125.6(6)$ K, no long-range order occurred until 23 K possibly due to moderate frustration in this triangular-lattice derivative. Our work shows an illustration that the use of mixed anions or anion-groups is beneficial to explore and discover novel materials with promising lattices and possible exotic physical phenomena.

Conflicts of interest

There are no conflicts to declare.

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Table of Contents Only

A 1/6th bond depleted triangular lattice has been experimentally realized in the novel compound $\text{PbFePO}_4\text{F}_2$ with moderately strong frustration.

