The structures and electronic properties of a number of real and hypothetical ABX$_2$ compounds sharing (or evolving from) a single P4/mmm structural type are examined. These include the known CaCuO$_2$ and SrFeO$_2$ phases. A number of variations of this P4/mmm ABX$_2$ framework, some obvious, some exotic, all with a chemical motivation, were investigated: A = alkali metal, alkaline earth metal or La, B = Ti, Fe, Cu, or Pt, and X = C, O, S, C$_2$H$_2$, or F. Careful attention was given to the d-orbital splitting patterns and magnetic states (ferromagnetic or antiferromagnetic) of these compounds, as well as their stability gauged by phonon dispersions and energetics. The most interesting as yet unmade compounds that emerged were (a) a carbide SrFe(C$_2$)$_2$, containing C$_2$ units with a C–C distance of 1.267 Å, (b) an AeTiO$_2$ series, with Ti–Ti bonding, part α, part π, tuned by the Ae$^{2+}$ cation size, and (c) NaPbF$_2$, for which a second structure was found, containing a hexagonal layering of (PbF$_2$)$^-$ molecules.

1. Introduction

An intriguing 4,6,8-connected tetragonal structure of ABX$_2$ stoichiometry was suggested by M. J. Bucknum, who termed it “Kentuckia”. Two views of the structure are shown: Figure 1 (top) is the primitive unit cell, P4/mmm. Figure 1 (bottom) shows the super cell, ($\sqrt{2} \times \sqrt{2} \times 1$), containing two ABX$_2$ units. The Wyckoff positions in the primitive unit cell are A (1/2, 1/2, 1/2), B (0, 0, 0), X (0, 1/2, 0), and X (1/2, 0, 0). Note the cubical coordination of atom A, the BX$_2$ sheets with a square-planar environment around B, and the 4+ quasi-octahedral coordination of X.

The primitive unit cell description in Figure 1 clearly shows the relationship of this structure to the familiar ABX$_2$ perovskite structure; the faint empty circles indicate where the atoms are missing relative to a true perovskite.

It turns out that a realization of the Kentuckia structure had been known for some time, in CaCuO$_2$. Containing typical alkaline copper oxides (AeCuO$_2$ with A = Sr or Ba) have been synthesized and investigated.

Recently, other systems crystallizing in this structural type have garnered attention. In a novel synthesis, LaNiO$_2$ was prepared by controlled H$_2$ reduction of the perovskite LaNiO$_3$, and in a similar preparation SrFeO$_2$ was synthesized via the reaction of the perovskite SrFeO$_3$ with CaH$_2$. SrFeO$_2$ contains planar FeO$_2$ layers with one Fe atom surrounded by four O atoms. Typically, Fe$^{2+}$ is either tetrahedrally or octahedrally coordinated, rarely in a square-planar environment, which is one reason for interest in this structure.

A number of theoretical studies have been published on these ABX$_2$ structures (CaCuO$_2$, SrFeO$_2$, LaNiO$_2$, and SrFeO$_2$) (P4/mmm, space group), typically employing density functional theory (DFT). These computations focused on the electronic structure and magnetism, thus requiring spin-polarized calculations. A variety of exchange-correlation

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energy functionals, such as LDA, GGA, DFT+U, and so forth have been applied in the calculations. As a result of the strongly correlated nature of transition metals, both the LDA and GGA methods fail to predict the correct magnetic ground state, but often obtain a reasonable approximation of the total density of states (TDOS). We will argue that the magnetism of these systems can be reliably calculated utilizing the local spin density approximation (LSDA) including on-site Coulomb interaction (U) (LSDA+U) method.

In this work we play the molecular slot machine by varying A, B, and X in this ABX$_2$ system. We do so not at random, but moved by chemical considerations. Careful attention is paid to the magnetic properties (ferromagnetic and antiferromagnetic) for all structures. We consider many different variations for A, B, and X in this framework; the most interesting, for a variety of reasons which will become clear later on, are CaCuO$_2$, SrFeO$_2$, SrTiO$_2$, SrFeC$_2$, SrFe(C$_2$)$_2$, SrFe(H$_2$)$_2$, and NaPtF$_2$. The first two exist; the other five are hypothetical compounds and potential synthetic targets. The calculated observables for all structures (lattice parameters, bond distance, magnetic moment, and electronic energy) are listed in the Supporting Information. Phonon dispersion is utilized to probe the dynamic stability of these compounds.

Let us begin with the known systems.

2. Predicting the Structural and Electronic Properties of ABX$_2$ Compounds

CaCuO$_2$. The environment of Cu in CaCuO$_2$ is square-planar. One expects a classical crystal field splitting for the d-block of four below one, the destabilized orbital being d$_{xy}$ (in the coordinate system defined in Figure 1). π-bonding may, and does, split the d$_{xz}$, d$_{yz}$, d$_{xy}$ block. The splitting pattern is confirmed by calculations on a molecular CuH$_2$ model (Supporting Information).

π-bonding between Cu d and O p orbitals would be expected to perturb this level pattern. The d$_{xy}$ orbital has greater possibilities for d-p π overlap, and should be pushed up relative to d$_{xz}$ + d$_{yz}$. We probed this with a [Cu(OH)$_4$]$^{2-}$ model and confirmed the effect (see Supporting Information). This model molecule proved to have its own complications, namely, holes in the oxygen p orbitals.

Let us see if these simple orbital ordering ideas are followed in the CaCuO$_2$ electronic structure. This is easiest to do in a spin-unpolarized system, so we first looked at the primitive cell of the spin-unpolarized CaCuO$_2$. For CaCuO$_2$, the calculated parameters (lattice constants $a = 3.842$ Å, $c = 3.195$ Å) agree with experiment $^{19}$ ($a = 3.856$ Å, $c = 3.181$ Å).

The band structure and the different contributions to the density of states (DOS) are shown in Figure 2. Between −6 and 3 eV, there are 10 filled bands, and 1 partially filled band at the Fermi level; these bands are due to the mixing of six O 2p orbitals with five Cu 3d orbitals. Above 3 eV, the unfilled bands can be assigned to Cu 4d orbitals. While the Vienna Ab-initio Simulation Package (VASP) orbital partitioning is unreliable (especially above the Fermi level), it is clear that, as expected, the partially filled band arises from the interaction between O 2p and Cu 3d$_{xy}$.

Let us take a closer look at the partially filled band in CaCuO$_2$. The orbitals contributing to the band crossed by the Fermi level are shown in Figure 2 at different special k-points in the Brillouin zone. The reason why the partially filled band in Figure 2 is at its highest energy at M is that the Cu 3d$_{xy}$ − O 2p antibonding interaction is minimized at M, maximal at X. The lesser, symmetry-allowed mixing of O 2s into the Γ and X orbitals is not shown here.

Returning to the basic orbital pattern seen in CaCuO$_2$, we focus on the individual orbital contributions in Figure 2 bottom. The d$_{xy}$ and d$_{x^2−y^2}$ bands appear in a two-peak pattern. It must be that they both interact with oxygen orbitals strongly, the aforementioned π-antibonding for d$_{xy}$, and σ interactions (as shown in Figure 3) for d$_{x^2−y^2}$. The higher-lying Cu d$_{x^2−y^2}$ − O 2p antibonding band gives rise to the states directly around the Fermi level.

To distinguish AFM and FM structures it is necessary to look at CaCuO$_2$ in a larger supercell, containing at least 4 CaCuO$_2$ units. In this model, the AFM structure is more stable than the FM structure by 0.18 eV per CaCuO$_2$. For AFM (CaCuO$_2$)$_4$ the calculated structure (lattice constants $a = 3.848$ Å, $c = 3.192$, magnetic moment $\mu = 0.29$ $\mu_B$) agrees pretty well with experiment $^{19}$ ($a = 3.856$ Å, $c = 3.181$ Å, magnetic moment $\mu = 0.51$ $\mu_B$). The calculated phonon dispersion of AFM CaCuO$_2$ shows no imaginary frequency modes, indicating the stability for the phase.

The supercell contains four formula units; thus the band structure will be 4-fold folded back, necessarily

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appearing more complex than for the spin-unpolarized system (see Supporting Information). Looking at the individual orbital contributions to the DOS (Figure 4), we see an expected distinction between spin states. To help distinguish between different spin-states (an arbitrary human assignment) we refer to the up or majority spin and down or minority spin. Most of the spin-unpolarized crystal field picture is retained: spin up and down $d_{z^2}, d_{xz} + d_{yz}$, and $d_{xy}$ bands are occupied. In the AFM supercell, we find that the Cu $d_{x^2-y^2}$ is responsible for the Cu contribution at the Fermi level.

Note that the spin polarization is nicely confined to the Cu states. The structural parameters and the Cu d orbital splitting ($z^2 < xz, yz < x^2-y^2$) of CaCuO$_2$ does not change noticeably from the spin-unpolarized primitive cell to the AFM supercell.

Our computations indicate that CaCuO$_2$ should be metallic, even if it has a low DOS at the Fermi level. This is not correct; experimentally it is known that CaCuO$_2$ is a semiconductor or insulator, with a 1.5 eV band gap.$^5$ As mentioned earlier, previous theoretical work on CaCuO$_2$ suggests that the LSDA fails to predict correct ground states because of the self-interaction item.$^{20}$ In our case, the LSDA+U exchange-correlation functional does locate the correct ground state (AFM) for CaCuO$_2$, but fails to provide us with the known insulating experimental electronic structure. Other calculations$^{10,15}$ employing non-plane-wave pseudopotentials, predict CaCuO$_2$ to be an insulator; still these calculations vary in both their band gap and the magnetic moment on Cu.

We tried to induce a band gap in our calculations by varying the Hubbard U and J terms, but these strategies do not work. We continue to look into this computational problem; while the failure to calculate CaCuO$_2$ as insulating is troubling, the DFT results seem reasonable for many of the other compounds we have explored.

**SrFeO$_2$.** Recently, an FeO$_2$ square planar layer was reported in the remarkable (because of its relationship to a perovskite) ternary SrFeO$_2$. Fe(II) in SrFeO$_2$ has three less valence electrons than Cu(II) in CaCuO$_2$. With six valence electrons on the metal one could imagine both high-spin and low-spin states for the system.

Our spin-polarized calculations for SrFeO$_2$ (four formula units per unit cell) indicate an AFM structure (0.11 eV per SrFeO$_2$ more favorable than the FM structure). The computed unit cell parameters in the AFM structure (lattice constants $a = 4.045$ Å, $c = 3.484$ Å) agree well with experiment ($a = 3.985$ Å, $c = 3.458$ Å).$^9$ The optimized Fe–O bond length is 2.022 Å, corresponding

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well to a variety of experimental Fe(II)–O distances: in an octahedral coordination (α-FeO), 2.171 Å;\(^{21}\) a distorted octahedron (α-Fe\(_2\)O\(_3\)), 1.946 Å to 2.116 Å;\(^{22}\) and in Fe\(_3\)O\(_4\) (tetrahedral and octahedral coordination), 1.886–2.060 Å.\(^{23}\) The calculated phonon dispersion shows no imaginary frequency modes.

The band structure and the different contributions to the DOS are shown in Figure 5. We can see from the computed band structure that SrFeO\(_2\) is a direct gap semiconductor (the smallest gap located at \(\Gamma\)). No physical measurements of the electronic properties of this phase appear have been published. The oxygen p states approach but do not cross the Fermi level. Each Fe 3d orbital is filled in the majority spin; the minority spin has only the 3d\(_{z^2}\) filled. Clearly, the computed SrFeO\(_2\) structure is high spin with four unpaired electrons, in agreement with experiment.\(^{9}\) Our computed magnetic moment is 3.7 \(\mu_B\), corresponding well to the experimental data\(^{7}\) (3.6 \(\mu_B\) at 10 K) and theoretical work.\(^{17,18}\) Essentially none of the spin polarization is felt by the oxides (see Supporting Information).

The large splitting of spin states for this magnetic metal center makes it difficult to assign a single level ordering diagram that would be appropriate for both spins. For instance, look at the contribution of d\(_{x^2-y^2}\) orbitals, they are at low energy for the majority spin, at high energy for the minority spin. Clearly all five d orbitals are occupied for the majority spin. The d\(_{z^2}\) orbital is the only one significantly occupied for the minority spin, but at relatively high energy for the majority spin.

The original experimental work on SrFeO\(_2\) assigned (apparently based solely on crystal field expectations) three electrons into the d\(_{xz}\) + d\(_{yz}\) set, as shown in Figure 6b. Subsequent theoretical work\(^{17,18}\) revised this assignment to have the d\(_{z^2}\) orbital doubly occupied, which is what we obtain in our calculation (Figure 6c). Very recently Kawakami et al. found a remarkable agreement with experiment.\(^{9}\)

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pressure-induced spin transition in SrFeO$_2$ from an antiferromagnetically coupled insulator to a ferromagnetic half-metallic state. We have not studied the latter state; for the former the spin densities reported are qualitatively similar to those we obtain.\(^{24}\)

The computed AFM CaCuO$_2$ d level splitting diagram \(z^2-x^2+y^2 < x^2-y^2 < x^2 + y^2\) (Figure 6a, with the \(x, y\) axes along the M–O bonds) was discussed earlier; it has the same ordering as SrFeO$_2$, but with three additional electrons. It needs to be said again that a single level splitting diagram combining majority and minority spins in one diagram for a highly magnetic material is a gross simplification: a comparison of the schematic of Figure 6 with the calculations of Figure 4 and 5 makes this clear. A similar splitting diagram (Figure 6b and c) was also discussed by Köhler.\(^{25}\)

Sulfur is in the same group as oxygen, so we explored SrFeS$_2$. The calculated SrFeS$_2$ AFM structure (lattice constants \(a = 4.853\) Å, \(c = 3.947\) Å) is 0.11 eV more favorable than the FM state. The replacement of O with the larger S caused the unit cell to expand in \(a\) and \(c\), as expected (computed SrFeO$_2$ lattice constants \(a = 4.045\) Å, \(c = 3.484\) Å). The computed TDOS (see Supporting Information) indicates that SrFeS$_2$ should be a semiconductor with a small gap, quite similar to SrFeO$_2$. However, the calculated phonon dispersion for SrFeO$_2$ gave imaginary frequency modes at \(\Gamma\) (~25\,\text{cm}^{-1}), indicative of possible structural instability (SrFeS$_2$ was also optimized and gave large imaginary frequencies). We did not search for a more stable structure. Note that only one ternary Sr–Fe–S compound is known.\(^{26}\)

SrFeC$_2$, SrFeC$_2$, a hypothetical phase, was formed by substituting \(\text{C}^{4-}\) for \(\text{O}^{2-}\). There are no reported ternary crystal structures of this elemental composition. Nor did we expect this structure to be viable; in it Fe would formally be \(\text{Fe}^{6+}\), not a typical oxidation state for the element. Still, out of curiosity, SrFeC$_2$ was optimized in the Kentuckia framework. To our surprise, the calculated phonon dispersion shows no imaginary frequency modes, indicating at least metastability for the phase.

Our spin-polarized calculations for SrFeC$_2$ (four formula units per unit cell) point to an AFM structure

\(0.65\) eV per SrFeC$_2$ more favorable than the FM structure. The computed SrFeC$_2$ unit cell parameters (lattice constants \(a = 3.777\) Å, \(c = 4.300\) Å, \(\mu = 2.40\) \(\mu_B\)) are very different than those calculated for SrFeO$_2$. The Fe–C distance is 1.888 Å, which falls within the expected range of Fe–C distances for many structures (see Supporting Information) in the Inorganic Crystal Structure Database (ICSD).

The C and Fe contributions to the DOS of SrFeC$_2$ are shown in Figure 7. We can see that SrFeC$_2$ is metallic. The magnetic moment calculated for Fe in SrFeC$_2$ (\(\mu = 2.40\) \(\mu_B\)) corresponds to roughly three unpaired electrons. Each Fe 3d orbital is filled in the majority spin; the minority spin has only the 3d$_{z^2}$ completely filled (the d$_{x^2}$ and d$_{y^2}$ are half-filled). Clearly, the oxidation state of Fe in the hypothetical SrFeC$_2$ is not +6, but closer to +2. There must be some carbon states unfilled because of electron transfer, and Figure 7 shows a good number of carbon states above the Fermi level.

Interestingly, a series of ABC$_2$ compounds exists, with a very different structure. In these, ScTi$_1$–C$_2$ (\(T = \text{Fe}, \text{Co}, \text{Ni}, x \sim 0.15\)), there are C$_2$ pairs with a C–C distance 1.35–1.40 Å.\(^{27}\) We thank a reviewer for bringing this structure to our attention.

SrFe(C$_2$)$_2$. A well-known (and industrially important) compound is CaC$_2$, which contains Ca$^{2+}$ and C$_2^{2-}$ acetylene units. This led us to think of substituting C$_2^{2-}$ units for O$_2^{2-}$ in SrFeO$_2$.

Transition metal carbides contain C$_2^{2-}$ units in a variety of orientations.\(^{28}\) We optimized three different “isomers” (Figure 8). The first isomer (Figure 8a) has the C$_2^{2-}$ units aligned along Fe–Fe, that is, ...Fe–C–C...–C–Fe... It also made sense also to try structures such as those shown in Figures 8b and 8c, differing from the first isomer by rotation of C$_2^{2-}$ units. The structure shown in Figure 8b has an interesting feature, ...CC...–C–C...–C–Fe... needles running through the structure, and \(\pi\)-coordination of C$_2^{2-}$ units to the irons. This \(\pi\)-coordination is also seen in the isomer of Figure 8c, as well as a potentially short C–C contact in the faces.

The FM state was favored in all three by ~0.11 eV per SrFe(C$_2$)$_2$ unit. The most stable (~1.3 eV per SrFe(C$_2$)$_2$ relative to the other structures) computed isomeric arrangement is shown in Figure 8a. The calculated unit cell parameters of FM SrFe(C$_2$)$_2$ are \(a = 5.058\) Å and \(c = 3.645\) Å; this yields a C–C distance of 1.267 Å and an Fe–C distance of 1.896 Å.

Can we understand the computed C–C distance in SrFe(C$_2$)$_2$, 1.267 Å, which is somewhere between acetylene, 1.20 Å, and ethene, 1.34 Å? Let us build up from a single C$_2^{2-}$ molecule to the carbon sublattice of SrFe(C$_2$)$_2$. Figure 9 shows a schematic molecular orbital diagram for a C$_2^{2-}$ molecule. The orbitals are familiar! For 10 valence electrons, C$_2^{2-}$, we note that the highest occupied molecular orbital (HOMO) is a nonbonding lone pair combination, 3g, and the lowest unoccupied molecular orbital (LUMO) is an antibonding orbital, 1g.$^*$.\(^{27}\)

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To help assign the orbital ordering in the extended material, single point DFT calculations of the C$_2^-$ molecule, maintaining the 1.267 Å C–C distances, were performed in a large unit cell (C$_2^-$ units separated by 10 Å) to avoid potential interactions between neighboring carbons. The band structure and DOS are shown in the Supporting Information. From this, we went to the C$_2^-$ sublattice isolated of the SrFe(C$_2$)$_2$ structure. In Figure 10, the DOS regions are labeled by their isolated molecular levels origin. The unit cell contains two C$_2^-$ molecules, which interact somewhat through space. As one would anticipate from the geometry of the structure (Figure 8) and the makeup of the C$_2^-$ orbitals (Figure 9), the $2\sigma_u^*$ and $3\sigma_g$ bands, made up from lone pairs pointing out from each molecule, are the ones most dispersed. Even at this stage we see that the bands arising from $3\sigma_g$ and $1\pi_g^*$ are just touching, so that $1\pi_g^*$ will begin to be occupied in the sublattice. The additional interactions due to mixing of C$_2^-$ states with Fe d orbitals in SrFe-(C$_2$)$_2$ must push some antibonding $1\pi_g^*$ states below the Fermi level. The net outcome is a C–C bond that is slightly longer than a typical triple bond.

The C–C separation in carbides ranges from 1.19 Å (in CaC$_2$) to 1.48 Å. The simple valence bond description of a range of C$_2$ reduction from C$_2^{2-}$ (triple bond) to C$_2^6^-$ (single bond) explains most but not all of this; a more detailed molecular orbital (MO) analysis, some of which we have done in our group, is needed. The 1.267 Å C–C distance computed makes sense for small occupation of the molecular $1\pi_g^*$ levels.

The total density of states (Figure 11) of SrFe(C$_2$)$_2$ differs from SrFeO$_2$. There is a large gap at the Fermi level in the majority spin, while the minority spin crosses the Fermi level. The material appears to be a half-metal. The computed magnetic moment on Fe is 2.4 $\mu_B$, which is lower than in SrFeO$_2$ (3.7 $\mu_B$) and corresponds roughly to three unpaired electrons (see Supporting Information). The partial density of states reveals that the Fe d ($d_{xz} + d_{yz}$) minority-spin states cover the Fermi level; there is also an interesting small contribution from C.

An interesting set of recently published compounds is Sc₃M(C₂)₂, with M = Fe, Co. In these, C₂ units (C–C = 1.45 Å) bridge square-planar M atoms, in a very different way from the structure shown in Figure 12. The C₂ units are significantly more electron-rich in Sc₃M(C₂)₂ than in our stoichiometry. We thank a reviewer for bringing these structures to our attention.

Utilizing the USPEX program, an evolutionary structure prediction, another structure of SrFeC₄ (P1) is obtained, still lower in energy. This is shown in Figure 13. The buckled FeC₄ sheets (Figure 13 right) consist of one-dimensional zigzag Fe–Fe chains (Fe–Fe = 2.52/2.50 Å) and dehydropentalene chains (C–C = 1.44–1.50 Å). The structure is more thermodynamically favored by 1.15 eV per SrFeC₄ than the Kentuckia SrFe(C₂)₂, and more stable by 0.64 eV than Cm SrFeC₄ obtained by annealing. However, the phonon dispersion calculation on this structure also did not converge. We are not absolutely sure that we have yet found the most stable SrFeC₂₂ geometry.

SrFe(H₂)₂. Straying even further from SrFe(C₂)₂, SrFe-(H₂)₂ was investigated. A quick search of the ICSD revealed no phases known containing only Sr, Fe, and H. If the H₂ units were intact, the oxidation state of Fe would be the unlikely −2 (there in Fe(CO)₄−2, but not in extended structures). So reduction of H₂ is likely. We found two structures by optimization from the Kentuckia-like geometries of Figure 8, and a more stable structure by an USPEX search. The two most stable phases are shown in Figure 14.

We focus our discussion on the more thermodynamically stable isomer, SrFeH₄ (Figure 14 left). In SrFeH₄, the AFM state (μ = 3.6 μµ) is favored over FM by 0.12 eV per formula unit. The structure is unusual, each Fe is involved in eight H bridges to other Fe ions; the Fe–H distance is 2.078 Å, which is within the range of a typical bridging Fe–H bond. Unfortunately, the phonon dispersion calculations on SrFeH₄ showed imaginary frequencies.

A dynamically stable structure emerged from the USPEX search, SrFeH₄ (USPEX) in Figure 14 right. Each Fe atom is bonded to two top H atoms (Fe–H = 1.77 and 1.92 Å) and four bridge H atoms (Fe–H = 2 × 1.86, 2 × 1.94 Å; Fe–H–Fe = 161°). The environment of an Fe atom in SrFeH₄ (USPEX) is approximately octahedral, and the d-electron count is formally 6. The magnetism (μ = 2.7 μµ) indicates that we do not have a simple “t₂g” below “e₉” octahedral splitting. Detailed analysis of the band structure (in the Supporting Information) indicates substantial covalence, Fe–H interactions, and an approximate dₓz₂dₓz−2dᵧz−1₁ configuration.

SrTiO₂. The Kentuckia ABX₂ structure can be thought of as a defect perovskite, as shown in Figure 1. Explaining other realizations of this structural type, we come to SrTiO₂, related to the classical SrTiO₃ perovskite.

Our spin-polarized calculations [For Ti, U = 4.5 and J = 0. Removing the Hubbard U from the calculation does not change the TDOS or phonon dispersion but decreases the Ti–Ti distance in the c direction (3.647 Å–3.589 Å). The different U terms, bond lengths, and DOS are located in the Supporting Information.] for SrTiO₂ (four formula

units per unit cell) indicate a nonmagnetic structure (μ = 0.00 μB, AFM and FM calculations identical). The computed SrTiO2 structure (lattice constants a = 4.036 Å, c = 3.647 Å) has a Ti–O distance of 2.018 Å, which falls well within the expected range of Ti–O distance for many structures (see Supporting Information) in the ICSD. Phonon dispersion calculations show no imaginary frequencies.

The band structure of SrTiO2 in a small window around the Fermi level is shown in Figure 15. The band structure immediately jumps out as unusual. The behavior of the levels along the Γ–Z direction is characteristic of a one-dimensional metallic chain.36,37 This was confirmed by calculation on two simplified one-dimensional models for AeTiO2: naked Ti2+ chains; and a [Ti(OH)4]2− model (Supporting Information). The dxy bands appear to almost touch the Fermi level but not to cross it. Yet, seven valence bands (2 × 3 for the O2− 2p, plus one for the Ti2+−) must be occupied, so in some regions of the Brillouin zone states that are not dz2 must be found below the Fermi level. The band structure shows that a degenerate dxy + dz2 band crosses the Fermi level, and is partially occupied.

The partially occupied band is made up of dxy + dz2, going down in energy from R–Γ. This bonding pattern is present in all the five Kentuckia phases studied.

The computed Ti–Ti distances are long, 3.647 Å, yet the partially occupied dz2 band hints at Ti–Ti bonding, part σ, part π (partial occupation of bonding dxz, dyz states). This led us to further investigation of this system.

If Ti–Ti bonding is present, why do not the layers come closer together upon optimization? We posited that it is the less glamorous (at least in this paper) alkaline earth metals that are responsible for halting the c direction contraction. We substituted Sr in SrTiO2 with two other alkaline earth metals, Ca (smaller radius than Sr) and Ba.

The Fermi level. The corresponding DOS is shown in the Supporting Information.

Table 1. Computed Lattice Constants (DFT), the Ti–Ti OP Values (eH), Magnetic States and Dynamic Stability (Based on Phonon Dispersion) in Five AeTiO₂

<table>
<thead>
<tr>
<th>Ae</th>
<th>(a(\text{Å}))</th>
<th>(c(\text{Å}) = \text{OP of Ti–Ti})</th>
<th>magnetic state</th>
<th>dynamically stable</th>
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<tr>
<td>Be</td>
<td>3.911</td>
<td>2.856</td>
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</tr>
<tr>
<td>Ba</td>
<td>4.075</td>
<td>4.129</td>
<td>0.23 FM</td>
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</tr>
</tbody>
</table>

(larger radius than Sr), to look for some sort of size-dependent trend (Table 1). As the ionic radii increase (Ca < Sr < Ba), the \(c\) direction expands significantly, indicating that the size of the alkaline earth metal plays an important role in determining the Ti–Ti distance. Phonon dispersion calculations of both CaTiO₂ and BaTiO₂ show no imaginary frequencies.

A still larger series of alkaline earth cations, \(A = \text{Be, Mg, Ca, and Ba}\), in ABX₂ provides a consistent picture (Table 1). Clearly, the alkaline earth metal plays a large role in tuning of the electronic properties of the material. The counterion also has an influence on stability: the Be and Mg compounds show imaginary frequencies and so may be unstable in this structure. The other counterions, Ca, Sr, and Ba, all are stable in a phonon study. The related perovskites BeTiO₃, MgTiO₃, CaTiO₃, SrTiO₃, and BaTiO₃ all exist experimentally. No defect ABX₂ analogues have yet been synthesized of any of these compounds, though we have recently made an attempt.

Note that for all of the compounds, there is Ti–Ti bonding as gauged by the OP values. Remarkably, this bonding is maintained even for quite long Ti–Ti separations. The electronic structure of this group of Ti⁺⁺⁺, d²⁻⁻⁻ compounds, shows metal–metal bonding in a partially ionic structure and that metal–metal bonding is tuned by surrounding cations. The situation is novel, and so we concentrated on providing a firmer basis for the existence of these phases in a separate paper. Here we just give the highlights of what we found.

First, several obvious reactions of the Kentuckia AeTiO₂ compounds were explored; they are decomposition to stable oxides AeO and TiO₂ and “burning” with O₂ to the corresponding perovskites. The first reaction is endothermic, the second exothermic.

We also explored a variety of alternative structures, based on chemical analogy, intuition, and an evolutionary structure searching algorithm. Given that CaO and TiO₂ go into a rock-salt structure, a “rock-salt” geometry (Figure 16) makes sense. Indeed such a structure is more stable than Kentuckia for \(Ae = \text{Be, Mg, and Ca}\). Still other less ordered variants (more details in the Supporting Information) of the rock salt motif come out of the evolutionary searching algorithm.

Kentuckia or rock-salt, the AeTiO₂ series is a fascinating group of structures with tunable Ti–Ti bonding.

NaPtF₂. Straying even further from CaCuO₂ or SrFeO₂, we looked at APTF₂, \(A = \text{Li, Na, K, and Cs}\). There are no reported compounds that combine these three elements, and the Pt oxidation state (formally +1) is unusual, which is one reason for our interest in this structure. Square planar coordination is typical of Pt(II), and so is stacking with Pt···Pt interactions, both in this oxidation state and in doped and oxidized compounds of the platinum blue type. The Kentuckia geometry offers the potential for realizing Pt–Pt bonding in an extended structure.

For NaPtF₂, the calculated AFM [For Pt, \(U = 7.5\) and \(J = 0\)] state (lattice constants \(a = 4.426\) Å, \(c = 3.042\) Å) is favored over the FM state by 0.05 eV per NaPtF₂. The Pt–F distance (2.213 Å) is longer than the average length (1.90 Å) observed in known solid state compounds (PtF₄, PtF₅, and PtF₆) and the sum of the atomic covalent radii (1.93 Å). The Pt–Pt separation along the \(c\) direction is 3.042 Å; longer than the 2.807 Å Pt–Pt distance in the bulk (fcc) Pt metal. This Pt–Pt distance is comparable with Pt–Pt separations between square planar platinum in the platinum blues (2.779–2.885 Å), in these compounds the oxidation state of Pt is fractionally greater than +2.

Compared with the optimized CaCuO₂ structure, NaPtF₂ appears “flattened” along the \(c\) direction; the

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**Figure 15.** Band structure (red dotted line) of nonmagnetic SrTiO₂ around the Fermi level (−2 to 2 eV) for SrTiO₂. The dotted line indicates the Fermi level. The corresponding DOS is shown in the Supporting Information.

**Figure 16.** Rock-salt type CaTiO₂ structure.

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$\alpha/c$ ratio is 1.46, larger than 1.21 in CaCuO$_2$. This may also be an indication of some Pt–Pt bonding along the $c$ direction. The total OP value for the Pt–Pt interaction in the $c$ direction is 0.05, a small net bonding effect. We also studied AFM LiPtF$_2$, KPtF$_2$, and CsPtF$_2$ (for the three structures, AFM is more favorable than FM) and found a general trend in Pt–Pt distance at the alkali metal was changed (Table 2). Like AeTiO$_2$, in the APTF$_2$, the spatial requirements of the largest cations (here Cs$^+$) break the weak Pt–Pt bond, moving the layers further apart. In phonon calculations, the Li and Cs compounds show imaginary frequencies, while the K variant is dynamically stable.

The band structure indicates that NaPtF$_2$ is semimetallic, with a tiny band gap, as shown in Supporting Information. The computed magnetic moment on Pt is 1.1 $\mu_B$, much larger than on Cu (0.29 $\mu_B$) in CaCuO$_2$. Comparing NaPtF$_2$ with CaCuO$_2$, while the magnetic moment is larger for Pt(I), the local spin population is very similar to that of Cu(II) with a hole in the $d_{x^2−y^2}$ orbit. Both are formally $d^8$ systems. We have no simple explanation yet for the difference in their magnetization.

The instability of NaPtF$_2$ in the $P4/mmm$ structure led us to explore MD annealing calculations on NaPtF$_2$. A new structure (space group: Ammm), shown in Figure 17, was reached. This NaPtF$_2$ phase, whose phonon spectrum showed no imaginary frequencies, is calculated to be 0.20 eV per NaPtF$_2$ more stable thermodynamically than the original $P4/mmm$ structure.

In the Ammm2 structure, the Pt atoms are in a distorted square-planar coordination, which can be viewed as the intersection of two 1-D chains. One chain has a Pt–F bond at 2.315 Å, F–Pt–F = 170°, in the other chain Pt–F is calculated as 2.250 Å, F–Pt–F = 175°. The computed magnetic moment on Pt in the FM state is 1.3 $\mu_B$, larger than in the Kentuckia framework (1.1 $\mu_B$).

There is a clear structural relationship between the new NaPtF$_2$ structure (Figure 17) and the $P4/mmm$ structure we began with. As Figure 17 and the text above describe, we have in the Ammm2 structure slightly corrugated and distorted PtF$_2$ planar sheets. But they are not placed directly above each other along $c$, as in the $P4/mmm$ structure. Instead, the layers slip relative to each other, so that a Pt of one layer is above a F of the next layer.

We moved next to evolutionary structure prediction, utilizing the USPEX program. Figure 18 (right) shows the lowest energy structure with the space group, $R\bar{3}m$. Each Pt atom is bonded to two F atoms (Pt–F = 2.00 Å, which is slightly longer than average Pt–F distance at 1.90 Å) and six Pt atoms (Pt–Pt = 3.07 Å). What we have effectively is a hexagonal sheet of (PtF$_2)^−$ units weakly bonded between the Pt’s. The phonon dispersion of the $R\bar{3}m$ NaPtF$_2$ indicates that it is dynamically stable. The structure is 0.76 eV per NaPtF$_2$ more favorable thermodynamically than the original $P4/mmm$ structure, and more stable by 0.56 eV than Ammm2 NaPtF$_2$ obtained by annealing. It may be that there are high energy barriers among these metastable structures, for they differ much. The computed magnetic moment on Pt in the FM state is 0.0 $\mu_B$, which is quite different with Kentuckia (1.1 $\mu_B$). And Ammm2 structure (1.3 $\mu_B$). The DOS are shown in the Supporting Information.

Given the crystallochemical similarity of fluoride (F$^−$) and hydride (H$^−$), we also investigated NaPtH$_2$ and obtained a similar structure, a hexagonal net of PtH$_2$− molecules. The band structure of nonmagnetic NaPtF$_2$ is shown in Figure 18 (right). NaPtH$_2$ is similar (see Supporting Information). Note the striking steep band crossing the Fermi Level. The slopes and positions of maxima in this band are in part a consequence of the primitive unit cell choice. This half-filled band is mainly Pt $d_x^2$, with some F (or H) admixture. This is consistent with the crystal field splitting in a $d^9$ linear PtF$_2^−$, in which one would expect a high-lying half-filled $d_3$. Linear PtH$_2$− units (one electron more) are known in the structure of Li$_2$PdH$_2$ and Na$_2$PdH$_2$ of Noréus et al.43,44

Interestingly a USPEX study of NaPtH$_2$ in a larger unit cell led us to still another defect perovskite structure, shown in Figure 19.

3. Conclusions

We have examined theoretically the structures and electronic properties of a variety of ABX$_2$ structures in the $P4/mmm$ Kentuckia family, including the known CaCuO$_2$ and SrFeO$_2$ compounds. The use of a supercell allowed us to compute correctly the magnetic properties of CaCuO$_2$ (it is AFM) but failed to give any band gap for this phase. For SrFeO$_2$, our calculations (and assigned $d$ orbital splitting) in general agree with previous theoretical work; we find the material to be a direct-gap semiconductor.

We also looked at a number of more atypical variations of this structure, all as yet unknown. These include SrFe$_2$C, SrFe$_2$(C$_2$)$_2$, SrFe(H$_2$)$_2$, SrFeO$_2$, and APTF$_2$. Among these the SrFe$_2$(C$_2$)$_2$, SrFeO$_2$, and NaPtF$_2$ phases were especially interesting. In a number of cases our structural search lead us quite far away from the parent Kentuckia structure.

The hypothetical carbide, SrFe$_2$(C$_2$)$_2$, contained C$_2$ units with a C–C distance of 1.267 Å. We were most surprised by the SrTiO$_2$ structure and its seemingly 1-D metallic behavior. A single band crosses the Fermi level in the $c$ direction (along $\Gamma−Z$). There is Ti–Ti $\sigma$ and $\pi$ bonding in this structure, even

at a Ti–Ti separation of 3.6 Å. That separation may be tuned by the alkaline earth ion; it is smaller for Mg, Be, and CaTiO2 and bigger for BaTiO2.

For NaPtF2 the Kentuckia structure showed some residual Pt–Pt bonding, but more interestingly, we found two more stable structures. One of these has a fascinating hexagonal sheet of weakly interacting (PtF2)− units.

A common feature among all compounds investigated is a partially filled d block. This leads to spin-polarization; most of the compounds we have examined (CaCuO2, SrFeO2, SrFeC2, SrFeS2, SrFe(H2)2, NaPtF2, LiPtF2, KPtF2, CsPtF2, SrPtO2, and LaPtO2) have antiferromagnetically coupled ground states. Only (SrFe(C2)2) was FM. An attempt was made to assign the d orbital splitting in the compounds studied. This proved problematic; the large splitting of spin states for many of the magnetic metal centers made it difficult to assign a single level ordering diagram that would be appropriate for both spins. Nevertheless, in this structural type most of the time we have a level pattern that puts the dx2−y2 level highest. The dxz level is sometimes below, sometimes above the dx2+dy2; the dxy states are in-between in energy.

The Kentuckia structure is not only the geometry of the known and interesting CaCuO2 and SrFeO2 phases, but leads to a number of other realizations with intriguing electronic properties.

### 4. Methods Summary

**DFT Method.** The calculations are based on the plane wave/pseudopotential approach using the computer program VASP45,46 employing the LSDA+U [The “LSDA+U” method for Fe with U = 4.5 eV and J = 0 on Fe17 predicted the correct ground state, U = 0 did not. For Cu, U = 7.5 eV and J = 0.] corrections47 of the PBE type, and the projected-augmented wave (PAW)48,49 method. All calculations included spin polarization, except as noted; also a √2 × √2 × 2 supercell, a 500 eV energy cutoff for plane waves and a (15 15 15) set of Monkhorst Pack grid of k-points. The supercell with four Cu or Fe atoms is the minimum cell that will allow for a computational distinction to be made between a ferromagnetic and an antiferromagnetic crystal. We allow all structural parameters (atomic position, lattice constants, and symmetry) to relax. Phonon calculations are carried out using VASP combined with PHON50 in a 2 × 2 × 2 supercell. The evolutionary algorithm USPEX51–53 was employed to find the lowest energy structures; the method has been successfully tested and applied to many other systems. The calculations were carried out at ∼0 GPa, consistent with our DFT calculations.

**Extended Hückel Theory.** After the structures are optimized with DFT, extended Hückel (eH)54 calculations are performed, utilizing the YAeHMOP program.55 The default extended Hückel parameters are employed. The eH calculations

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**References:**

55. Landrum, G. A. nviewkel (ver 3.0). nviewkel is distributed as part of the YAeHMOP extended Hückel molecular orbital package and is freely available on the WWW at http://overlap.chem.cornell.edu:8080/YAeHMOP.html
are certainly less reliable for structures, but offer a number of analytical tools for exploring the nature of bonding. With the DFT program we use, it is difficult to get reliable atomic and orbital contributions to the density of states (DOS).\textsuperscript{56}

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Supporting Information Available: The calculated parameters, the band structures and DOS, phonon dispersion, and the impact of different Hubbard U values. This material is available free of charge via the Internet at http://pubs.acs.org.

\textsuperscript{56} The RWIGS values are the default parameters from the pseudopotential file. There are real problems with VASP projected DOS values not adding up to the total DOS.