Materials 218/Chemistry 277: Take home final

Date: March 13, 2019; Due date: March 19, 2019 (slip under Ram’s door by 5:00 pm)

Please properly attribute the source of any material you might make use of (URLs, references . . . ) Also, do please read this exam sheet very carefully!

Important References


Questions

1. Fascinating properties have been discovered in compounds with the ThCr$_2$Si$_2$ structure type ("122" structure) with the generic formula, $AM_2X_2$. Some of these compounds have $A = \text{Ca}^{2+}$, $X = \text{P}$, and $M$ is a (formally divalent) 3$d$ transition metal (i.e. $\text{Fe}^{2+}$, $\text{Co}^{2+}$, $\text{Ni}^{2+}$). Sketch the structures of CaFe$_2$P$_2$, CaCo$_2$P$_2$, and CaNi$_2$P$_2$ in VESTA: Space group $I4/mmm$ (#139), Ca = (0,0,0); $B$ = (0,0.5,0.25); $P$ = (0,0,$z$) using the data tabulated below. Is there a centering operation in this space group? [4]

<table>
<thead>
<tr>
<th>Compound</th>
<th>$a$ (Å)</th>
<th>$c$ (Å)</th>
<th>$z$ (P)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaFe$_2$P$_2$</td>
<td>3.855</td>
<td>9.985</td>
<td>0.3643</td>
</tr>
<tr>
<td>CaCo$_2$P$_2$</td>
<td>3.858</td>
<td>9.593</td>
<td>0.3721</td>
</tr>
<tr>
<td>CaNi$_2$P$_2$</td>
<td>3.916</td>
<td>9.363</td>
<td>0.3774</td>
</tr>
</tbody>
</table>


3. Draw the electrostatic valence net for CaFe$_2$P$_2$ assuming the formal valences of $\text{Ca}^{2+}$, $\text{Fe}^{2+}$, and $\text{P}^{3−}$. Do the charges balance? [4]

4. What are the bond valence sums for Ca and Fe in CaFe$_2$P$_2$? Can you infer anything about the nature of bonding in, and between the layers? Use $B = 0.37$, and $R_0 = 2.27$ Å for Fe–P and $R_0 = 2.55$ Å for Ca–P bonds. [4]

5. Below are the calculated densities of states for CaFe$_2$P$_2$, CaCo$_2$P$_2$, and CaNi$_2$P$_2$. Label regions with major contributions from the $M$–$d$ ($t_2$ and $e$ levels), and P–$p$ orbitals. [5]

6. Would you expect metallic conductivity in any of these compounds? For the metallic compounds, where do the metallic states come from ($M$ or $P$)? Why? What does this tell you about the nature of bonding of the metal atoms in the layers? [5]
7. Which compound is likely to be magnetic in light of the Stoner criterion for itinerant magnetism and how can you tell? [2]

8. Read the paper by Hoffman and Cheng (Ref. [1]). In their analysis of the stacking of $[\text{Mn}_2\text{P}_2]^{2-}$ layers, they observe strongly localized $p_z$ orbitals projecting into the interlayer space. According to the authors, why do the P-P distances contract as one moves across the periodic table ($M = \text{Fe}$ to Co to Ni)? Explain with a sketch of the energies of the $p_z$ bonding/antibonding orbitals relative to the $d$ bands and the Fermi level. [5]

9. How would the substitution of Ge for P change the $X-X$ distance (e.g. $\text{SrCo}_2(P_{1-x}\text{Ge}_x)_2$)? Discuss in the context of Hoffman & Cheng. Describe the conclusion drawn by S. Jia et al. (2011) in Ref. [3] for $\text{SrCo}_2(P_{0.5}\text{Ge}_{0.5})_2$ with a sketch of the DOS for the $X-X\sigma^*$ and Co $3d$ orbitals relative to the Fermi energy. Reminder: chemical potential $\approx E_F$. Would you expect this compound to be magnetic in light of the Stoner criterion? [6]