Materials 218/Chemistry 277: Take home final

Date: March 11, 2015; Due date: March 18, 2015 (slip under Ram's door)

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

1. R. Hoffman and C. Zheng, *J. Phys. Chem.* **89** (1985) 4175–4181. [**doi**]

2. S. Jia, S. Chi, J. W. Lynn, and R. J. Cava, *Phys. Rev. B* **81** (2010) 214446. [**doi**]

3. S. Jia, P. Jiramongkolchai, M. R. Suchomel, B. H. Toby, J. G. Checkelsky, N. P. Ong, and R. J. Cava, *Nature Phys.* **7** (2011) 207–210. [**doi**]

Questions

1. Fascinating properties have been discovered in compounds with the $ThCr_2Si_2$ structure type ("122" structure) with the generic formula, AM_2X_2. Some of these compounds have $A = Ca^{2+}$, $X = P$, and M is a (formally divalent) $3d$ transition metal (*i.e.* Fe^{2+}, Co^{2+}, Ni^{2+}). Sketch the structures of $CaFe_2P_2$, $CaCo_2P_2$, and $CaNi_2P_2$ 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]

Compound	a (Å)	c (Å)	z (P)
$CaFe_2P_2$	3.855	9.985	0.3643
$CaCo_2P_2$	3.858	9.593	0.3721
$CaNi_2P_2$	3.916	9.363	0.3774

   A. Mewis, *Z. Naturforsch. B* **35** (1980) 141–145.

2. What are the coordination geometries of the M and P atoms (coordination numbers, M–P–M and P–M–P bond angles, bond lengths)? What is the shortest interlayer P–P distance in the three compounds? [4]

3. Draw the electrostatic valence net for $CaFe_2P_2$ assuming the formal valences of Ca^{2+}, Fe^{2+}, and P^{3-}. Do the charges balance? [4]

4. What are the bond valence sums for Ca and Fe in $CaFe_2P_2$? 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. [5]

5. Below are the calculated densities of states for $CaFe_2P_2$, $CaCo_2P_2$, and $CaNi_2P_2$. 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]

CaM_2P_2
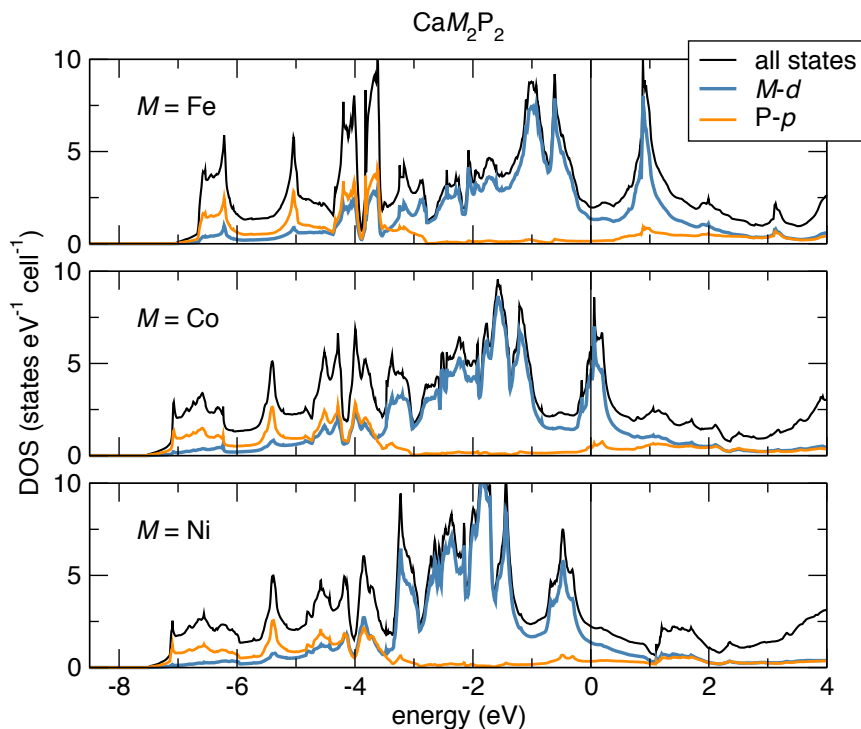
7. Which compound is likely to be magnetic in light of the Stoner criterion for itinerant magnetism and how can you tell? [2]

8. Read the paper by Hoffman and Cheng (Ref. [1]). In their analysis of the stacking of $[Mn_2P_2]^{2-}$ layers, they observe strongly localized P 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 = Fe to Co to Ni)? Explain with a sketch of the energies of the P 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.* $SrCo_2(P_{1-x}Ge_x)_2$)? Discuss in the context of Hoffman & Cheng. Describe the conclusion drawn by S. Jia *et al.* (2011) in Ref. [3] for $SrCo_2(P_{0.5}Ge_{0.5})_2$ with a sketch of the DOS for the X–X σ^* 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]