Materials 218/Chemistry 277: Assignment 4

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This is last year's midterm

1. The compound whose structure is given below is a superconductor with a transition temperature of 8.5 K [He *et al. Nature* **411** (2001) 54]. Examine the structural information provided below and answer the questions that follow:

   Space group $Pm\bar{3}m$ (No. 221: $P\ 4/m\ \bar{3}\ 2/m$) a = 3.8122 Å.

Atom	Wyckoff	x	y	z
Mg	$1a$	0	0	0
Ni	$3c$	$\frac{1}{2}$	$\frac{1}{2}$	0
C	$1b$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$

   Note: You should NOT require space group tables.

   (a) What is the formula of the compound ? [1]

   (b) Explain P, $4/m$, $\bar{3}$, and $2/m$ in the complete space group symbol. Sketch the rotation axes on a cube. [2]

   (c) Sketch the various sections in the structure. [1]

   (d) What is the structure type formed just from Mg and C? Sketch the whole unit cell of this structure with just Mg and C. [1]

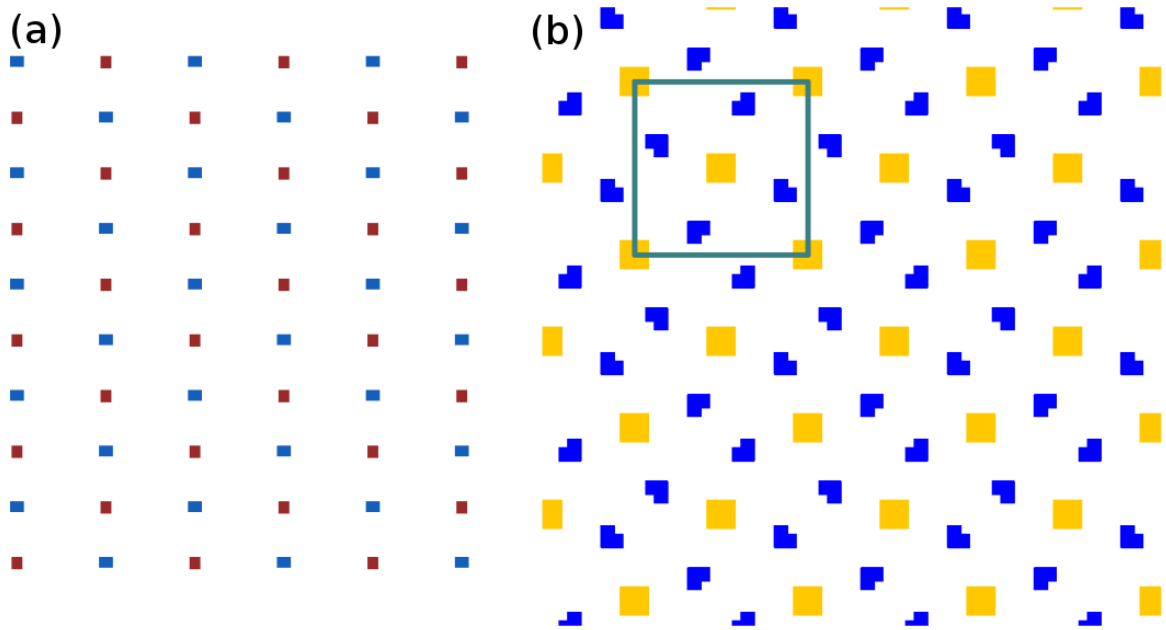
   (e) Can you interchange the positions of Mg and C without changing the structure (Yes or No)? [1]

   (f) What is the coordination of Mg in terms of Ni (distance and number of neighbors)? [1]

   (g) What is the coordination of C in terms of Ni (distance and number of neighbors)? [1]

   (h) Tile the layer (at least 3×3) at $z = 0 = 1$ with only Ni indicated, and identify an *fcc* sublattice. What would the unit cell edge of the *fcc* lattice be in terms of a = 3.8122 Å? [1]

   (i) The answer is ? [1]



2. In the Figure (a) above:

   (a) Sketch the unit cell boundary. [1]
   (b) What is the ratio of the two motifs in the structure? [1]
   (c) What kind of 2D lattice is depicted? [1]
   (d) What is the plane group? [1]

3. In the Figure (b) above:

   (a) What is the ratio of the two motifs in the unit cell? [1]
   (b) What is the highest order rotation axis that can be identified? Locate its position(s). [1]
   (c) Locate mirror and glide planes if present, in the unit cell. [2]
   (d) What is the plane group? [1]

4. Electrostatic valence rule:

   (a) The electrostatic valence rule of Pauling states:

   $$\Sigma s = -V_- \text{ and } s = V_+/Z$$

   where s is the bond valence, V_+ is the charge (valence) of the cation, V_- is the charge of the anion, and Z is the coordination number of the cation. If $Z = 4$ in amorphous SiO_2, how many Si is each O bonded to. Sketch the bond valence net. Note charges: Si^{4+} and O^{2-}. [2]

   (b) Describe the Si–O network in amorphous SiO_2 with a sketch. [2]

   (c) The addition of H_2O to SiO_2 (as happens in certain hydrothermal processes in geology) results in the Si–O–Si network of silica being broken. Use electrostatic valence to determine the H_2O:SiO_2 ratio required so that all SiO_4 tetrahedra are *isolated*, *ie.* there remain no Si–O–Si linkages. Sketch the bond valence net of this hydrated species. [2]

   (d) If Z were 6 for Si in SiO_2 (giving SiO_6 octahedra as in mineral stishovite SiO_2) how many Si would O be bonded to ? Sketch the bond valence net. [2]

   (e) TiN crystallizes in the rock-salt structure: If TiN comprises Ti^{4+} and N^{3-}, does the electrostatic valence rule apply? What is wrong, the rule or the assigned charge? [2]