Chemistry 208—Spring 2009 **Problem Set 2**
Professor K. N. Raymond **Answer Key**

1.
To find the density of the crystalline sample, you must find the density of the solvent mixture in which the sample is suspended. Note that this is *not calculable with the information given.* At the point of suspension, the density of the mixture is equal to the density of the crystal.

To determine the density of the solvent mixture, draw off a known volume and weight it. This allows the calculation of the crystal density.

$$\rho_{mix} = \rho_{xtal}, \quad \left(\quad \rho_{mix} = \frac{m_{mix}}{V_{mix}}, \quad \rho_{xtal} = \frac{m_{xtal}}{V_{xtal}} \right)$$

In order to convert this to a formula weight for the compound you must know the unit cell volume (V_{cell}) and the number of molecules in each unit cell (Z). Because the crystal is orthorhombic, V_{cell} = abc. Calculation of the formula weight for your compound is most easily derived from the formula for density:

$$\rho = m / v$$

Because the density of the crystal is the same throughout, we can solve this equation using the mass and volume of the unit cell. Because the mass of the unit cell will be the formula weight multiplied by the number of molecules in each cell, this equation becomes:

$$\rho = \frac{m_{cell}}{V_{cell}} = \frac{Z \bullet FW}{abc}$$

Solving for the formula weight, we have $FW = \dfrac{\rho \bullet abc}{Z}$.

2.*a)* To get the magnitude and phase angle of the resulting vector, the real components are added (the apparent x-axis):

$$12\cos(45) + 8\cos(100) \approx 16.36$$

The y ('imaginary') component:

$$12\sin(45) + 8\sin(100) \approx 7.10$$

Calculation of the length of the vector with coordinates (16.36, 7.10) gives a magnitude of 17.83 and a phase angle of 66.5°.

$$| F |^2 = \sqrt{x^2 + y^2} \approx 17.83$$

$$\tan\phi = y / x = \frac{7.10}{16.36}$$

$$\phi = 66.5^o$$

b)Choose one of the waves as the reference phase. (This solution will choose wave **A**). Then let α be the difference in phase between the two waves and F = **A**+**B**:

$$F = F_1 \cos\phi + F_2 \cos(\phi + \alpha)$$

By differentiating, we can find when the function is at a maximum (or minimum)

$$\left(\frac{\partial F}{\partial \phi}\right)_{\phi_{max}} = -F_1 \sin\phi - F_2 \sin(\phi + \alpha) = 0$$

Rearranging, we get a more useful expression $\dfrac{\sin(\phi+\alpha)}{\sin\phi} = -\dfrac{F_1}{F_2}$

Using of the sum/difference formula $\sin(\phi+\alpha) = \sin\phi\cos\alpha + \sin\alpha\cos\phi$ and remembering that $\cot\phi = \dfrac{\cos\phi}{\sin\phi}$, we can write the equation as

$$\cos\alpha + \cot\varphi \sin\alpha = -\frac{F_1}{F_2}$$

Solving for the phase angle, we get $\cot\phi = \dfrac{-\left(\dfrac{F_1}{F_2} + \cos\alpha\right)}{\sin\alpha}$

We can now substitute in our values for F_1 (12) and F_2 (8) as well as α (55).

$$\cot\phi = \frac{-\left(\dfrac{10}{8} + \cos 45\right)}{\sin 45}$$
$$\phi = 21.5$$

But remember that our function for *F* had a phase shift of 45°, so we must add 45° to return to the proper frame of reference, making the phase shift of $F_1 + F_2 = 66.5°$.

To obtain the magnitude, we substitute this phase angle back into the original equation

$$F = 12\cos(66.5 - 45) + 8\cos(66.5 - 100) = 17.83$$

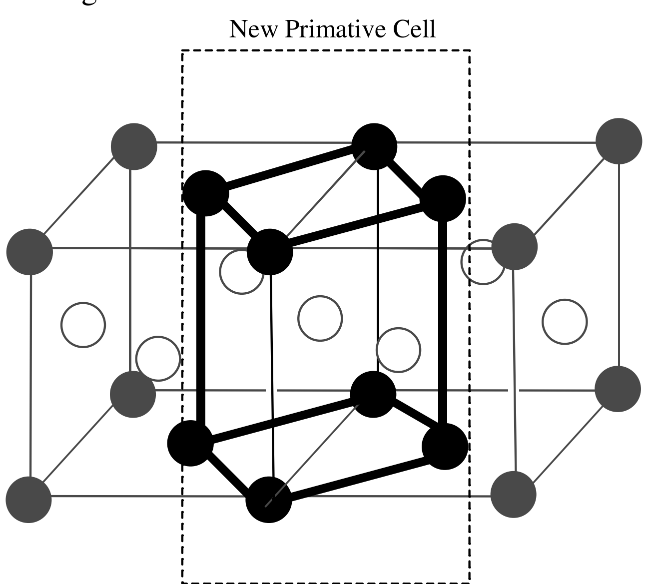
c) The two waves are now completely out of phase (180° phase shift) and will interfere destructively. The problem is trivial because the magnitude of wave **B** can simply be subtracted from **A** and the phase shift will be unchanged, giving a magnitude of 4 with a phase shift of 45°. This is *destructive interference*.

3.

Space group	Unit cell	Point Symmetry	Laue Symmetry
$P2_12_12_1$	Orthorhombic	mm2	mmm
$P2_1/m$	Monoclinic	2/m	2/m
$P\bar{1}$	Triclinic	1	$\bar{1}$
P4nc	Tetragonal	4mm	4/mmm
P1	Triclinic	1	$\bar{1}$
Pccm	Orthorhombic	mmm	mmm
Amm2	Orthorhombic	mm2	mmm
P31c	Trigonal	3m	$\bar{3}$m1
Fm$\bar{3}$	Cubic	m$\bar{3}$	m$\bar{3}$

4.

The new primitive cell has one-half the volume of the centered cell. The new cell is still tetragonal.



Space group: P4/mmm (#123)
Atom positions:

Gold:	0,0,0	1,0,0
	0,0,1	1,1,0
	0,1,0	1,0,1
	0,1,1	1,1,1

Cu: ½,½,½,

5.

$$\vec{a}^* = \frac{\vec{b}\times\vec{c}}{V} \qquad \vec{b}^* = \frac{\vec{c}\times\vec{a}}{V} \qquad \vec{c}^* = \frac{\vec{a}\times\vec{b}}{V}$$

$$V^* = \vec{a}^*\cdot(\vec{b}^*\times\vec{c}^*) = \left(\frac{\vec{b}\times\vec{c}}{V}\right)\cdot\left[\left(\frac{\vec{c}\times\vec{a}}{V}\right)\times\left(\frac{\vec{a}\times\vec{b}}{V}\right)\right]$$

$$V^* = \left(\frac{1}{V^3}\right)(\vec{b}\times\vec{c})\cdot\left[(\vec{c}\times\vec{a})\times(\vec{a}\times\vec{b})\right]$$

Two useful properties of vector cross products are:

$$\vec{u} \times \vec{u} = 0$$

$$(\vec{u} \times \vec{v}) \times (\vec{w} \times \vec{z}) = (\vec{u} \cdot \vec{v} \times \vec{z})\vec{w} - (\vec{u} \cdot \vec{v} \times \vec{w})\vec{z}$$

Using these properties in the above equation for V^*, we get

$$V^* = \left(\frac{1}{V^3}\right)(\vec{b} \times \vec{c}) \cdot \left[(\vec{c} \cdot \vec{a} \times \vec{b})\vec{a} - (\vec{c} \cdot \vec{a} \times \vec{a})\vec{b}\right]$$

$$V^* = \left(\frac{1}{V^3}\right)(\vec{b} \times \vec{c}) \cdot \left[(\vec{c} \cdot \vec{a} \times \vec{b})\vec{a}\right]$$

But we know that

$$\vec{c} \times \vec{c}^* = \left(\frac{1}{V}\right)\vec{c} \cdot (\vec{a} \times \vec{b})$$

$$\vec{c} \times \vec{c}^* = 1 \Rightarrow V = \vec{c} \cdot (\vec{a} \times \vec{b})$$

$$\Rightarrow V^* = \left(\frac{1}{V^3}\right)\left(\vec{b} \times \vec{c}\right) \cdot (V\vec{a}) = \left(\frac{1}{V^2}\right)\left(\vec{b} \times \vec{c}\right) \cdot \vec{a}$$

Furthermore, we know that dot products commute (i.e. $\vec{u} \cdot \vec{v} = \vec{v} \cdot \vec{u}$), so

$$(\vec{b} \times \vec{c}) \cdot \vec{a} = \vec{a} \cdot (\vec{b} \times \vec{c}) = V$$

$$\Rightarrow V^* = \left(\frac{1}{V^2}\right) \cdot V$$

$$\therefore V^* = \frac{1}{V}$$

Another way to approach this is using metric tensors. Note that V^2 equals the determinant of the metric tensor and the inverse of the metric tensor is the metric tensor of the reciprocal cell. Therefore, its determinant is equal to the square of the reciprocal cell volume which then equals $1/V^2$.

The cross product of **b** and **c** is the area of the parallelogram which they define.