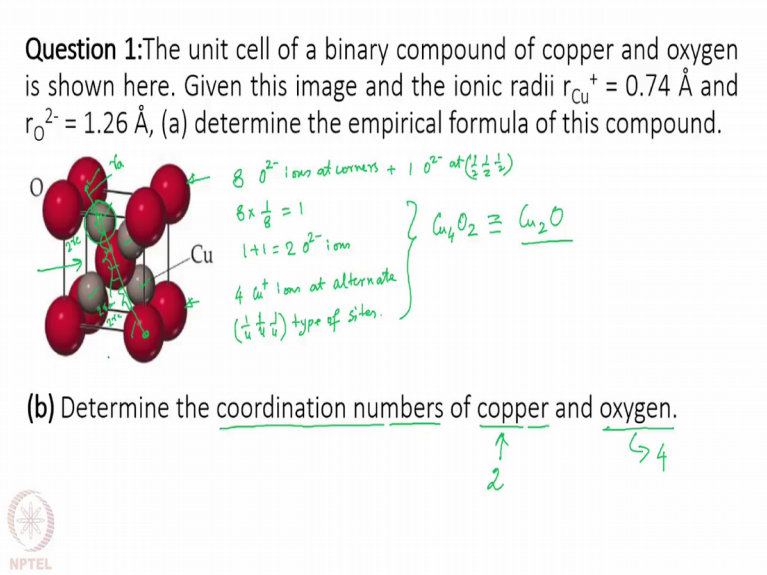
Chemical Crystallography
Prof. Angshuman Roy Choudhury
Department of Chemical Sciences
Indian Institute of Science Education and Research, Mohali

Lecture – 26
Tutorial - 4

Welcome to this course of Chemical Crystallography. In this lecture, I am going to discuss the solutions to the problems given in the Assignment 4. So, the 1st problem that is given here is based on a structure of copper oxide.

(Refer Slide Time: 00:27)



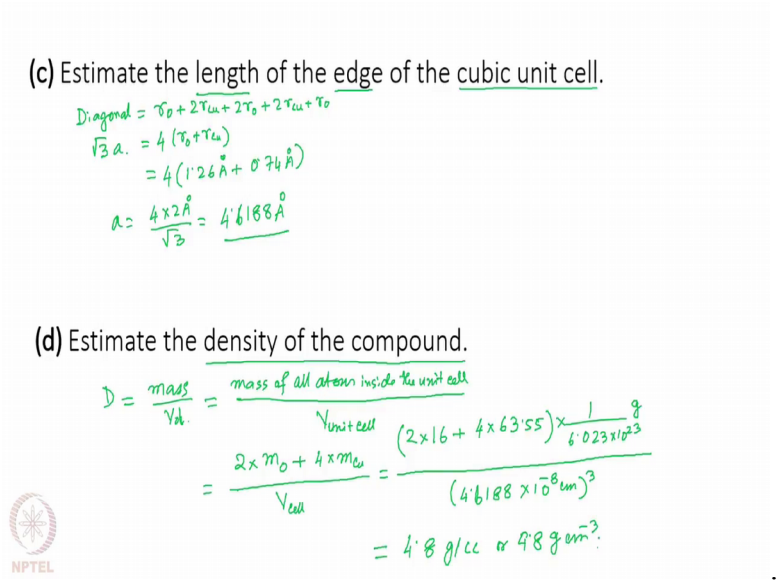
So, the question is: the unit cell of binary compound of copper and oxygen is shown here. Given this image and the ionic radii of copper as 0.74 angstrom and red oxide as 1.26 angstrom, determine the empirical formula of this compound.

So, what you could see here is that the unit cell that is drawn as oxygen at corner positions; so 8 corners have 8 oxygens and each oxygen is 1 each contributing to the Cu. So, you have 8 O 2 minus ions at corners. So, they contribute one 8 each. So, 8 into one-eighth is equal to 1 plus you have 1 oxygen at the center. So, you have oxide ions at corners plus 1 O 2 minus at half half half which means you have 1 plus 1 2 O 2 minus ions in the unit cell and it is clearly visible that there are 4 copper ions Cu 2 plus ions Cu plus ions, sorry Cu plus ions.

So, you have 4 Cu plus ions at alternate one-fourth type of sites which means if it is there at one-fourth, it is not there at one-fourth half one-fourth things like that. So, you have 4 full copper ions and 2 oxide ions. So, it corresponds to a formula like Cu4O2 which is equivalent to Cu2O. So, this is the empirical formula of the compound that is shown here in the structure.

Now, determine the coordination number of copper and oxygen. If we look at the central oxygen, we see that there are 4 coppers nearby and this is true for all oxygens. If you grow the lattice in all 3 directions, so coordination number for oxygen is 4. Now, if you look at the structure more carefully what we see is for every copper you have only 2 oxides nearby. So, the coordination number for copper is just 2.

(Refer Slide Time: 03:53)



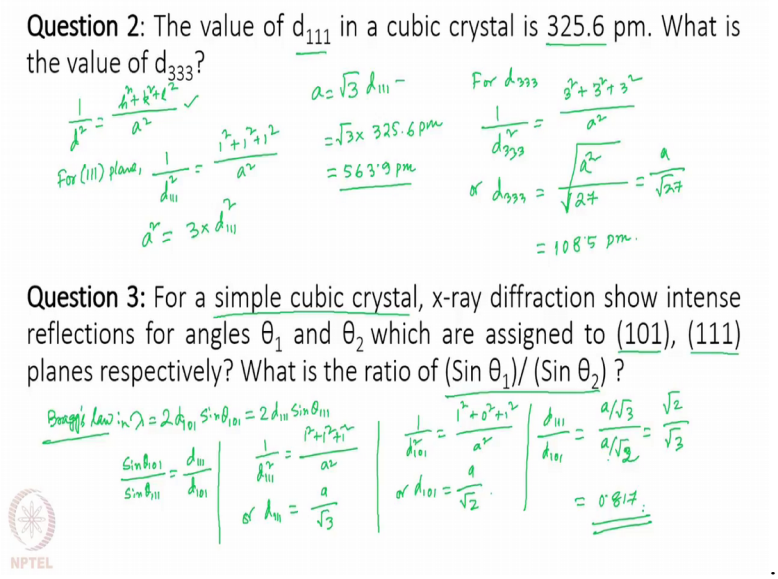
Now, the next question is estimate the length of the edges of the cubic unit cell. So, what we see here is that, this particular structure has a packing along the diagonal in such a way that you have r anion, this point is 2 r cation, this part is again 2 r anion, this part is 2 r cation, and this is again r anon.

So, if we add all that is the diagonal is nothing, but r 0 plus 2rcu. Sorry, r cation plus r oxygen plus r copper plus 2 r oxygen plus 2 r copper plus r oxygen which is equivalent to 4 times r o plus r c u and this is nothing, but equal to the diagonal which is root 3 a. So, now the values for r o and r c are given r o is 1.26 angstrom and r c u is 0.74 angstrom which means a equal to 4 into 2 angstrom by root 3 which is equal to 4.6188 angstroms, the edge length.

So, when we try to estimate the density of this compound, what we need is the density D is equal to mass by volume. What is this mass of all the atoms inside the lattice? All atoms inside the unit cell divided by the volume of the unit cell which means we are talking about 2 into mass of oxygen atom plus 4 into mass of copper atom divided by V cell.

So, we can write as it as 2 into 16 which is atomic weight of oxygen plus 4 into 63.55 which is atomic weight of copper. This is the molar mass. So, mass of one atom is divided by Avogadro number divided by the total volume of the unit cell which is 4.6188 into 10 to the power minus 8 centimeter whole cube. So, if you calculate this number, this density which should turn out to be 4.8 gram, this is gram per cc or 4.8 gram per centimeter cube.

(Refer Slide Time: 08:15)



The question number 2 is based on the formula that you one can derive from simple Bragg's law for a cubic cell that 1 by d square is equal to h square plus a square plus l square by a square for 111 plane. We write 1 by d 111 square is equal to 1 square plus1 square plus 1 square by a square and this d 111 is given. So, we can write a square equal to 3 into d 111 square or simply a equal to root 3 d 111. So, that means it is equal to root 3 into 325.6 pico meter is equal to 563.9 pico meter.

So, now we write the same equation for d 333 1 by d 333 square is equal to 3 square plus 3 square plus 3 square by a square or d 333 is equal to a square by 27 square root which means it is a by root 27 which is nothing, but 108.5 pico meter. The question number 3 says that it is a simple cubic crystal which is important information. Here, to get the values for d 101 and d

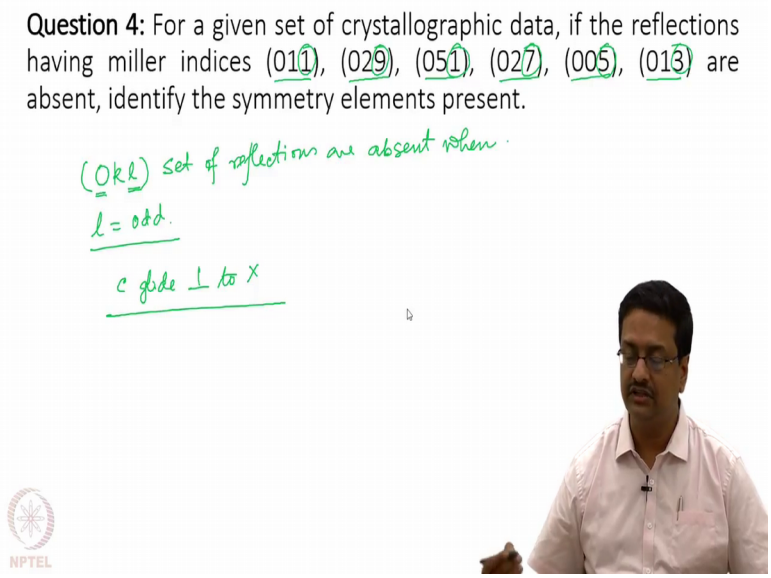
111, we should be able to write the Bragg's law for these two reflections n lambda is equal to 2 d 101 Sin theta 101 is equal to 2 d 111 Sin theta 111.

So, that means if we want to calculate the value of Sin theta 101 by Sin theta 111, we need to calculate the ratio d 111 by d 101 0. So, how do we do that? We write again 1 by d 111 square is equal to 1 square plus 1 square plus 1 square divided by a square or d 111 is nothing, but a by root 3 and similarly, 1 by d 101 square is equal to 1 square plus 0 square plus 1 square by a square or d 101 is nothing, but a by root 2.

So, if I try to do d 111 by d 101 is nothing, but a by root 3 divided by a by root 2. So, it is equal to root 2 by root 3 which is equal to 0.817. So, this is the ratio of Sin theta 1 by Sin theta 2 for this particular crystal.

The 4th problem here: that has the question on systematic absence. The question is for a given set of crystallographic data is the reflections having miller indices 011, 029, 051, 027, 005, 013 etcetera are absent identify the symmetry element present. On observing these reflections if you can clearly see that the 0 k l set of reflections are absent, when l is odd you see 191753 with all values of l being odd are absent. This means that it is a glide plane because in case of screw axis, 2 indices are 0 whether it is h 00 or 0 k 0 or 00l represent 21 screw, but here it is 0 k l. That means, it is a kind of mirror which is a glide and the absent condition says that l is odd which means it is a C glide perpendicular to X. So, this systematic absence condition indicates a C glide perpendicular to X.

(Refer Slide Time: 12:52)



So, you should be able to then identify these systematic absence conditions given if the condition say the systematic you should be able to analyze this systematic absence conditions. And then, it comes to a conclusion that what kind of symmetry element is present in the lattice.