

PROFESSOR: Why don't we get started. Good afternoon-- to stretch the literal meaning of the word considerably. What a miserable day out there.

I get to and from the boonies via the commuter rail. And this morning, we sat there for an hour part way in because a tree had fallen across the railroad track. I don't know who went out to do it, but somebody had to get a saw and saw the tree up and take it off the tracks before we could proceed into Boston.

Even with that, I was sort of reluctant to get off the train. I saw how it was pouring outside. So I am highly flattered that you decided to trudge through the puddles and show up this afternoon.

All right, this is a momentous occasion because we are exactly at this point, halfway through the term. And this is when we are about to change gears from our discussion of symmetry theory and switch over to physical properties of crystals and the way in which symmetry impacts on those properties.

What I wanted to do primarily today, though, is to say a little bit in a very fast and very simple way about the nature of crystal structures because that is one of the primary uses of symmetry theory. It's to describe the periodic arrangements and symmetrical arrangements of atoms in crystals. So it's the language that's necessary to describe such arrangements, particularly when they're beyond the red balls at the corner of the cube and black balls in the middle of the faces level of structure.

Let me first, for your amusement and edification, pass out another problem set. This has only two problems on it. You are not really equipped to do it yet because we haven't talked about space groups. So don't worry about doing that now. But I wanted to get it in your hand so that you could look it over.

It's a good problem set on which to end this part of the discussion-- but there's another one that I'll be passing out next week-- because this is an example of how

you can use the notions of symmetry that we have established to say some fairly profound and non-obvious things about the nature of atomic arrangements. So that's the purpose of this problem set. It is to give you an opportunity to see the surprising things that can fall out of our material that we now have at our disposal.

Let me begin by telling you where we left off last time. We had completed deriving the so-called Bravais lattices, the three-dimensional space lattices. The process by which we did this was to take our two-dimensional space groups, the plane groups, and say that, if we add a third translation, we will have generated a space lattice.

But these different nets in the base of the cell are special and determined by the fact that there are symmetry in these nets. So if we take, for example, a net that is exactly square-- it's square because there's a fourfold axis there. And that fourfold axis, in a space lattice, pokes not only into the base of the cell but extends up through space.

So you must pick a third translation such that the symmetry elements line up. We would take each of the crystallographic plane groups and pick a third translation. You end up with almost all of the lattices that you're going to get except for the ones that involve cubic symmetries that are inherently three-dimensional.

And the reason for that is that the more complex three-dimensional point groups are, for the most part, obtained by adding inversion to the simple symmetries that exist in two dimensions. But inversion doesn't require anything of a lattice. So you can immediately say that $2M$ and $2/M$ are compatible with the same sort of space lattice because the symmetry $2/M$ is nothing more than what you get when you add inversion to either a twofold axis or a mirror plane.

And, finally, another way of classifying crystals, and a broader way of classifying them, is according to the coordinate systems that are necessary to describe the lattices. And these are called the crystal systems.

And, as a mnemonic device for keeping straight what the crystal systems are as opposed to the crystal classes, which is another word that we haven't used but it's

another word for the point groups, the crystal systems goes with coordinate systems. And it's simply a word to describe the shape of the lattices, family of lattices, that we've described.

And we distributed a handout last time that gave the names of these systems and the relations that exist between the edges of the unit cell, which we use as the basis for our coordinate system and also the labels that we put on them.

I have another sheet, which I'll pass around, which is nothing new. It just assembles-- I'll give you two sheets, which I'll pass around. The first is an assembly of the crystallographic point groups in a somewhat neater and tidier way than we had on the sheet that we passed around last time. So this is a picture of all 32 of the point groups.

Again, beware of the fact that mirror planes and guides to the eye that split things up into 90 degree segments or 60 degree segments come out deceptively similar on these sheets. But there with the representative pattern are the arrangements of symmetry elements, a representative pattern of motifs, and the international and [INAUDIBLE] symbol for all 32 of the three-dimensional point groups.

And then the next sheet I'll pass around takes the point groups and groups them together with the lattices that can accommodate them and the crystal system that describes the arrangement of axes in the lattice. So this is, in a nutshell, everything that we've covered up to this point.

And, at this point, I have to say that there is some disagreement on how many crystal systems exist. And even though people who work with symmetry and mathematics are usually rational, almost to a fault logical individuals, there are several junctures as you build up a body of knowledge where you could go either way or adopt either convention. You sort of got to pay your money and take your choice.

And this occurs in our arrangement of point groups and lattices among the crystal systems. This occurs in the hexagonal crystal system. Symmetry 3 and the other

point groups that can be derived from it can be placed either in a hexagonal lattice, that is to say, a third translation C that is exactly at right angles to a pair of translations, A_1 and A_2 , which are 120 degrees apart.

Or a three-fold symmetry can go into this funny double-body centered hexagonal lattice, which could be defined, if we were masochistic and enjoyed working in an oblique coordinate system, could be defined instead in terms of a rhombohedral lattice, which had the special characteristics that three translations are identical by symmetry, called therefore A_1 , A_2 , and A_3 ; and the angles between the more equal α_1 , α_2 , α_3 ; and they could be anything we wished.

So that is a unique sort of crystal system and unique sort of coordinate system. There are those who would say that if this is the case, we really have seven crystal systems-- triclinic; monoclinic; orthorhombic; tetragonal; hexagonal; and then this one that is compatible only with a three-fold axis and that is called the trigonal system or, by some folks, the rhombohedral system; and then, finally, the cubic.

Well isn't that a rational and logical thing to do? Yeah, question at this point?

AUDIENCE: Do you have any extra copies of the sheet [INAUDIBLE]

PROFESSOR: Oh, yes. There should be more than enough floating around. This one here?

[? AUDIENCE: The ?] [? chart ?]

AUDIENCE: Yeah, [? not the ?] [? chart ?].

PROFESSOR: OK. I'll give you-- I think there are more back there. But why don't you take one for now?

Yeah, so it's a perfectly reasonable thing to do is to set up the trigonal system as a separate coordinate system to describe the rhombohedral lattice. The problem that creates, however, is that if you do this, there is no longer any one to one correspondence between the point groups and the crystal systems.

A crystal with symmetry 3, for example, can fit into it either in a hexagonal lattice or

a trigonal lattice. US So sometimes a crystal with point group 3 would have to be called a hexagonal crystal, sometimes a trigonal system. But which is it? Well it can be either. So admitting the trigonal system as a separate crystal system breaks down the one to one correspondence between point groups and crystal systems.

The very pragmatic reason for not admitting the trigonal system as a separate crystal system

is that, although you can in this funny triple hexagonal cell define a primitive trigonal cell that has a special geometry, nobody in their right mind, as I indicated earlier, would want to work in such a coordinate system. Better to take the triple cell, pay the price of three-fold redundancy, and yet have two interaxial angles that are 90 degrees and one that's specialized at 120. That's a much more convenient reference system for our description of crystal properties.

One final thing I'll comment on but won't say anything about very much-- I always do that. I say I won't say anything about it but, and then launch into a 10 minute digression. Off in the right hand corner is something called the Laue group of which there are 11.

The Laue groups are those of the point groups that contain the operation of inversion. And the reason they're called the Laue groups is that one of the primary ways, other than looking at crystal morphology to determine the symmetries of a crystal, is to look at the way it diffracts x-rays.

So if we had, for example a tetragonal crystal and there were lattice planes in here that were related by 90 degree rotations, then if we brought in an x-ray beam at such an angle to satisfy Bragg's law and saw some sort of intensity that came off, if we rotated the x-ray beam 90 degrees, we ought to see diffraction at the same angle and with exactly the same intensity. So either by moving the x-ray beam, or simpler thing would be to leave the x-ray beam fixed, since it's attached to an x-ray generator that weighs a ton or more, instead move the crystal relative to the x-ray beam.

Now what would you do in this way of thinking to determine whether a crystal had the operation of inversion in it? If this is the set of planes with indices HKL, you, again, would bring in an x-ray beam at an angle θ , in out.

Look at the intensity from the set of points HKL. And then look at diffraction, both in terms of the Bragg angle θ and in terms of the intensity. Look at that diffraction from the planes that were related to HKL by symmetry.

Well what plane is related to HKL by symmetry? It's these planes down here which have indices minus H, minus K, minus L.

So if we did the corresponding experiment to what I did to the left, we'd bring in an x-ray beam like this. It would be diffracted at some angle θ . And we'd look at the intensity for the set of planes minus H, minus K, minus L.

Is that going to be any different? No. Right-minded person would say, why should this intensity be different? All we're doing is bouncing the x-ray beam off the opposite side of one in the same set of lattice planes. So why should the intensity be any different? In this case, clearly if the set of lattice points is rotated by some finite angle, we are not going to see equivalent diffraction from planes that are 90 degrees apart.

So the upshot is that the diffraction symmetry of a crystal, the way in which planes with indices that are related by symmetry diffract in terms of position of the beam and intensity, the diffraction symmetry of a crystal always looks as though that crystal possessed an inversion center.

So, therefore, to-- and I qualify this by saying, to a good approximation-- the only point groups that you could determine and distinguish from one another by x-ray diffraction are the point groups that contain an inversion center. Almost, but not quite. If we look a little more closely at what is doing the scattering, it is not the Bragg planes. These are imaginary, shimmering, absolutely planar things that are constructs that we use to interpret the process called diffraction.

Inside the crystal what is actually doing the diffraction is a collection of atoms, each

of which are scattering the x-radiation. And that physically is what causes the diffraction. And the resultant intensity is the addition of all the little wavelets scattered by these separate atoms.

So in terms of the atomistics of what is involved, to look at diffraction from the set of planes HKL and contrast that with the diffraction for the set of planes minus H, minus K, minus L, we're coming in from opposite directions. And here the beam would hit-- let's call the atoms, if I did not do so already, let's call them A and B. A for a and b for big.

Diffraction from the set of points HKL would pass through the sheets of A atoms first and then impinge on the B atoms, whereas in the opposite direction, the x-ray beams would impinge upon the B atoms first and then hit the A atoms. Does that make a difference? Aha. Believe it or not, it does.

And I can't explain why without going into a very detailed discussion of diffraction. But if you compare the intensities that are scattered by these two sets of planes, which are related by inversion and therefore just opposite sides of one another, it does make a difference which atom the x-ray beam encounters first.

And the difference in intensity is on the order of 3% to 5%, although by picking a radiation appropriately for the particular chemical species in the crystal, you could increase this perhaps to 10% or 12%. But that is something that you could not do until synchrotron radiation came along, which could actually tune the wavelength to a particular value that you wish to use and not use something that was spewed out by an x-ray tube that had a target such as molybdenum or copper or chromium, perhaps.

OK, so you can with this careful measurement of intensity distinguished between the opposite sides of the given set of Bragg planes, unless, of course, the crystal did have inversion in it. And then there would be no difference at all.

It requires a very careful experiment, though, because there are many things that could make the intensities different. For example, absorption by the crystal. If the

crystal has an irregular shape, the absorption, which can easily be factors 10, 20, or even more, the absorption would be different for x-ray beams coming in those two orientations.

So in any case, as I say, I won't say anything about it. But 10 minutes later, that's the meaning of the Laue groups. These are the point groups that have inversion in them.

That effect that I just described, by the way, is called anomalous scattering or anomalous dispersion. There's really nothing anomalous about it at all. It has to do with the way electromagnetic radiation interacts with the clouds of electrons that are distributed about the nucleus of each atom.

Where we will go from here to finish up symmetry theory will be to now take the 32 crystallographic point groups and to drop those point groups into each of the distinct 14 Bravais lattices. And then we'll need combination theorems to deduce where the additional symmetry elements arrive. And when we go through that process, if we were to do this exhaustively, we would find that there are 230 distinct three-dimensional symmetries that involve point group symmetry operations and lattice type.

I saw several faces blanch. Don't worry. We're not going to do that. What we will do next time is do a small handful and then conclude by showing you how this information is tabulated in the international tables.

And the quick, immediate answer to that question is that the problem set that I passed around has two pages for two different point groups that show the way that this information is tabulated in the international tables. So that's where we'll end up. And we'll come pretty close to completing that when we meet on Thursday.

I heard no sighs of relief. I heard no cheers. So you are presumably still engaged in this material somewhat.

I have two things I would like to do. We talked about crystal systems and point groups. And let me now ask, do you think there is a crystal known for every one of

the point groups? Think so? I saw some skeptical shakes of the head. The answer is yes, but just barely for some of the point groups.

One of the very rare point groups, in terms of structures that populate it, is our high symmetries but which lack inversion or mirror planes. One very, very rare point group is 432-- just axes arranged in a cubic arrangement with no mirror planes or inversion centers.

And my rationalization of that is that if an arrangement of atoms has to conform to all of these rotational symmetries, it's pretty hard for it to do it and have that assemblage of atoms assume the lowest possible energy state if it doesn't pick up in the process inversion or mirror planes as additional symmetry element. Sort of satisfying for me. But that's not a rigorous argument.

OK, let me now take a poll. Do you think, using the broader cut of the crystal systems, do you think there's a crystal known for every crystal system? Are there triclinic, monoclinic, orthorhombic, tetragonal, trigonal, hexagonal, cubic crystals known? Yeah. That's a pretty realistic expectation. And that is indeed the case.

But now let me cut this a little finer. Which do you think is the most popular crystal systems for real materials and which do you think is the rarest? OK. Who thinks triclinic crystals are the most common? OK, there are pessimists.

What is the definition of a pessimist? The pessimist is somebody you should borrow money from because they'll never expect to be paid back.

Who would say cubic crystals? There are naive [? optimists. ?] Now I will reveal all.

The answer is, it depends. Depends upon whether you're talking about, interestingly, inorganic materials or whether you're talking about organic materials.

If you look at inorganic materials, the most popular crystal systems are-- and the results are, first of all, cubic. Is this not a benign world in which we live. Most inorganic materials-- if you're a material scientist who works with metals and with ceramics, you're going to work with cubic materials, thank God, most of the time.

The second most popular-- by a considerable margin but there are still a lot of them-- is orthorhombic. And the third most popular, shortly behind orthorhombic and almost in a tie, monoclinic and tetragonal.

We'll launch into a quick overview of crystal symmetry. And we'll see why inorganic materials have high symmetry. It's true, in particular, when the material is held together by ionic bonding. If the bonding is ionic, it's non-directional and atoms of opposite charge will therefore try to get as close as possible to the atoms of opposite charge.

And because atoms of like charge repel one another, the surrounding atoms will try to be as widely separated as possible. And this grouping of atoms, positive around negative, tends to have a lot of symmetry. And, therefore, the way in which these groups are linked together has a lot of symmetry.

OK, I said organic materials. And I'll pass around some actual numbers that were assembled a long time ago but are still, in terms of proportion, still valid. The organic compounds are broken down into whether these are compounds based on rings or extended, lopsided molecules. And the numbers are very different depending on that.

But, for organic molecules [? material, ?] monoclinic is the most common, then orthorhombic. And shortly after orthorhombic comes way, way behind is tetragonal and triclinic, which are almost tied.

And I think I can rationalize this observation, as well. Organic materials contain discrete molecules. And if we've got something-- and I'm going to, since I know I'm among friends, display my abysmal ignorance of organic chemistry. I am unapologetically and unabashedly inorganic and even non-metallic in my research interests.

So let's suppose we have something that's composed of various strange rings with little side groups sticking off like this, another one off like this, and then maybe another ring up like this. That, to me, looks like a reasonable molecule in terms of

my ignorance of organic chemistry.

So if there are these finite groups and you're going to put them together in a crystal, what are you going to try to do? They're going to be held together by very weak van der Waals forces, which are non-directional. So think of the outline of this molecule as being some ugly thing like a ham hock. And then your problem, if the forces between these molecules are non-directional, how do you close pack ham hocks?

The way you would do it would be to put down a row of them in a close-packed sequence. So we'll put down things that look like this. And then, maybe to make them fit together, dovetail another one in here. And maybe something like that.

And then for the next row down, and you would maybe put the nose of one in here. And then put the other one in here, the nose of one here, and something like that-- being very schematic. The lattice that describes this packing is not going to be orthogonal. It's not going to be square with high symmetry or even have two orthogonal translations.

It's going to be something that has this as translations. There's going to be an A and a B that is not at right angles to it. And the B translation will have different links, simply because the thing that you're putting together in close packing has a very irregular shape.

So I think that is the reason why molecules, discrete molecules that try to achieve something that is as close packed as possible, will have translations in them that are of unequal length and making arbitrary angles with respect to one another.

So having kept you guessing for so long, let me pass out another sheet. This was a compilation that was done a long time ago. And there were only 9,000 crystals for which complete crystallographic data had been obtained. This was way back in 1967.

As I say, there's much more data now, easily in order of magnitude. But I don't think the proportions will change very much. They'll stay about the same. Let me pass out these sheets.

So make sure you memorize them because the first question on the next quiz is, how many out of 8,759 crystals are actually triclinic? I would never do that.

All right, any comments or questions? Yes, sir.

AUDIENCE: Why would organic molecules of such odd shapes even be crystalline to begin with? Why wouldn't they just be amorphous?

PROFESSOR: OK. Clearly the interatomic forces are very directional and very strong. And that's going to hold the molecule into a fixed configuration.

AUDIENCE: Didn't you say there were van der Waals forces?

PROFESSOR: But they're these-- even for something that is not ionic or metallic, there still are weak attractive forces between these molecules. Why? Well, the charges are not uniformly distributed over these molecules. So there are going to be some van der Waals forces that tend to hold them together.

And a van der Waals force is essentially non-directional. So if you have this weak force, you're going to be able to squish the crystal into something amorphous very easily. And organic materials are usually very subject to plastic deformation.

But if you assemble the molecules carefully from solution, or by vaporization, condensation, they're going to want the order if they are solidified with enough mobility to rearrange themselves in the lowest energy configuration.

I think what you're saying is these are not going to be very strongly bonded crystals. They're going to melt at low temperatures. But, nevertheless, prepare them properly, and the lowest energy state will be ordered.

AUDIENCE: I'm sure [? they're ordered. ?] But would it be such that you have [? translational ?] symmetry? Who's to say it's going to have a definite pattern that will repeat itself?

PROFESSOR: Yeah, if there are attractive forces-- let me again use a hand-waving argument. If you've got a bunch of particles and they aggregate here in the lowest energy

configuration, that is going to be the lowest energy configuration. And a similar group of atoms will want to do the same thing here. And if there are interactions between these groups, they're going to arrange themselves in an order configuration.

That is simply saying-- this is a very weak qualitative argument-- says if you have a configuration which is the lowest energy arrangement here, any other place in the system where those atoms get together and congeal are going to assume that same configuration. OK?

Other comments or questions? This is all very qualitative but actually concerns matters that we are describing a language to describe.

AUDIENCE: [INAUDIBLE]

Yes, there are. If you look at this table that came around, if you look at cubic organic materials out of-- there-- what is the number? 117 out of what looks to be several thousand. Yes, there are cubic organic crystals, but very few in number. Hexagonal- - 56 out of a rather large number.

All right, when we took a poll a week and a half or so ago and said, how many of you had seen any material and crystal chemistry in solid state chemistry in a previous class on structure and bonding or crystal chemistry, and only a few people tentatively twitched a hand slightly. So what I'd like to do for the rest of this session, since this is what symmetry theory is developed to describe, I'd like to say something about structures and why they form the way they do to give some qualitative insight.

This is a fat pack of notes. And I'll go over it quickly with you and lead you by the hand through it. But this is not material for which I'll hold you responsible.

In fact, I'll turn my back and those who want to get home early because of the rain can tiptoe out. And I won't even notice who you are unless everybody goes. And then I'll feel very hurt because I wrote these out. And it took a lot of trouble.

All right. I have to apologize and say that most of what is described in these notes applies to ionic bonding and, to a lesser extent but still in large measure, to metallic structures. And what is the reason for that? It's because the metallic bond, to a fair approximation, an ionic bond rigorously, if you believe Coulomb's law, is a non-directional sort of bonding.

So the structures that are assumed, the structures that are the lowest energy configuration turn out to be determined by interatomic distances and ionic or metallic sizes. The Coulombic interaction that holds ionic compounds together is a central force. And one of the features of electromagnetism is that, if you have some distribution of charge about center and another distribution of charge of a different sort about a another center, the cohesive force between, let's say, a positive ion and a negative ion is, along a line, joining their centers.

And, secondly, you can take, once you're outside the distribution of charge, you can clump all the charge together at the center of the distribution. So that's what makes the ionic bond so simple. And that's why everybody who talks about bonding and structure discusses ionic bonding because organic chemistry is just too complex in comparison.

So let's look at a given cation. And cations generally tend to be smaller than anions because you've removed electrons from the outer configuration. We'll look at some effective sizes of ions in just a bit. But you've stripped electrons off to make a positively charged ion. You've added electrons on to make a negatively charged ion. So when you add electrons, the ion functions has [? always ?] had a larger radius.

So let's bring up a B minus ion as a neighbor. And for those two species, there will be, if we put energy as a function of separation D , there's going to be a Coulombic attractive force that goes as $1/D$.

But when the electron configurations get in to close proximity, at small separations, the electrons will start to push one another, beginning with the outer electrons first, into higher energy states. And the energy of interaction, due to the interaction of orbitals, will increase the energy of the system.

And the result then is that the net potential, as a function of distance for an isolated ion pair-- I was looking for some colored chalk and it's gone-- is something that rises steeply at low separations and then levels out more gradually at larger separations. So this then would be an equilibrium separation, D_0 , for that ionic pair.

If we got energy out, and for that isolated ionic pair it'll be just exactly this much energy, E_0 . If it weren't for a pair of ions-- let's take another A and bring it into the system. And there's a lot of room to put still another A around. And we can add that to the system.

And every time we bring up an additional neighbor, we get approximately this much energy out of the system. But not quite because there will also be repulsive interactions between the ions of like charge. OK? But to a good approximation to within about 10% to be quantitatively, every time we bring up another neighbor, we get out the same amount of energy again by forming this group.

And all that works splendidly until-- let me now look at the arrangement of anions about the little cation because they will have to have a shell as well. So if we have a small cation and we bring up a big fat anion, there will be, first of all, two consequences.

These ions of like charge will interact repulsively. So the lowest energy situation is going to be one in which these neighboring ions arrange themselves so that the repulsive energy is minimized. And we're going to get the maximum separation between all of these anions and get the minimum energy when they arrange themselves on the corners of a regular polyhedron.

And that's where symmetry starts to come in to the importance of ionic structures. That, for this particular configuration of anions, the B ions might be on the corners. And I am not drawing them in contact now just so it'll be easier to draw. The B ions will be equidistant and tend to arrange themselves on the corner of the regular polyhedron.

If we got energy up by bringing up extra neighbors, we will reach a point where the

B ions will essentially be in contact. And the A ion is rattling around in a hole. It can touch perhaps two neighbors. And we will get the full amount of energy on.

But for the other two neighbors, we're going to be out here on this curve. And we won't get nearly as much energy out. But at the same time, we're paying the price energetically of all of these repulsive interactions between the surrounding neighbors of like charge.

So the second consideration is that, as we said, first of all, this group of atoms, which is referred to as a coordination polyhedron, it first of all will be symmetric. And then the number of neighbors, the number of ions of one charge that are coordinating the others-- and that's something called the coordination number, introduce some jargon-- has an upper limit that is going to be determined by the size of the ions.

So these are the two basic tenets of ionic crystal chemistry. So having established those points, we can do some geometry and assume that the ions are hard spheres or at least elastic spheres with some stiffness because it's going to take energy to perturb the orbitals of the electrons and, just in terms of simple geometry, calculate the range of radius ratios R_A/R_B where A is the central ion in the polyhedron and B is the surrounding ion, and do this for different coordination numbers, picking polyhedra in which the surrounding ions of like charge are as widely separated as possible.

So starting at the beginning, coordination number one would be a pair of ions. Obviously no constraints whatsoever on the relative sizes. R_A/R_B can be anywhere it likes between zero and infinity.

For coordination number two, again the surrounding ions want to be as widely separated as possible. So it'll be a linear chain. But, again, the central ion can become as small or as large as it like. So the range of radii is between zero and infinity.

For coordination number three, the polyhedron will be an equilateral triangle. And if

you calculate the geometry, when the B ions are exactly in contact, you have a little 30, 60, 90 triangle in which one edge of the triangle is RB and the other is RA plus RB. And you can manipulate that into the form where you can show that there will be a lower limit RA/RB , which is 2 over the square root of 3 minus 1 . And that turns out to be a magic number, 0.155 .

Going to coordination number four, you'd say, aha. That's going to be square group. No, a square group would not keep the surrounding ions of like charge as widely separated as possible. And the geometry which would keep them as widely separated as possible but yet in contact with the central sphere would be a tetrahedron. The Bs would be arranged on alternating vertices of a cube. The magic number there turns out to be 0.225 .

Coordination five-- very, very rare. Five is a crystallographic abomination because five-fold symmetry does not conform to a lattice. But there would be, in principle, one five-fold group. And that would be a trigonal prism where you have three Bs arranged on an equilateral triangle about the central A. And then you have one A up here, another B up here, and another B down here.

So this, then, is a bipyramid, a triangular bipyramid. And you can derive a range of radius ratios for this. And this is a dandy problem to give on a problem set. But you find that the range of radius ratios RA/RB is the same as for six-fold coordination, which is the next one considered on the handout.

So we six coordination with the corners on a regular arrangement would be an octahedron. And the permitted range there is 0.732 to infinity. Five coordination, the trigonal prism, leads to exactly the same range of radii. And the reason is, if you look at the geometries, this triangle here is the same for both an octahedral coordination and a trigonal pyramidal coordination.

Notice as we chug on that the lower limit to the radius ratio is gradually increasing. And if we go to coordination number eight, cubic coordination, it goes up to 1 to infinity. And for coordination number 12 , RA/RB has to be exactly 1 period. And that would be what you achieved in the close-packed number.

OK, turning the page. There is also going to be a range of radius ratios that's determined by the number of As that can be packed around a central B. And doing exactly the same calculation, if, for example, four-fold coordination permitted in terms of R_A/R_B , the range is 0.225 to infinity.

If we want to know the limits for packing of A around B with tetrahedral coordination, this would give us numbers R_A/R_B that were exactly the same range of numbers because we've just changed the labels. If we want to put everything on the same basis, in terms of one particular radius ratio, if we do anion to cation radius ratio, the range would be 0.225 to infinity.

If we take the reciprocals of these numbers for four-fold coordination of B, this would be $1/0.225$ to $1/\infty$. So this will give us-- this is zero. This is infinity. So there'll be a range of radius ratios, $0.225 < R_A/R_B < 1/0.225$, which turns out to be 4.44.

So this would be the range of permitted radius ratios for $CNA = 4$ and $CNB = 4$. So there's going to be an upper limit that's imposed by the packing of As around B and a lower limit that's imposed by the packing of Bs around A.

But what are going to be the coordination numbers of A and B? Let me finish this up. And then we can take our break.

I'm going to now restrict things rather drastically. I'm going to consider binary compounds in which all cations have the same coordination and all anions with the same coordination. And the implication there is there's only one type of coordination number for both. And that's not always true in compounds.

Sometimes you find a given species that has two different coordination numbers in a more complex compound. If that's the case, if this is the A ion and this is the B ion, let me consider the chemical composition of a bond. And that's going to translate into the same thing as the compound.

So let's suppose there's a number of Bs around the As, which is, by definition, the coordination number of A, and a number of As around a B and that is, by definition, the coordination number of B. So let me look at a wedge that's associated with this bond. And this is an amount of an A atom, which is 1 over the coordination number of A.

And if I do the same thing for the B ion the part of the B ion associated with one bond is going to be 1 over the coordination number of B. So we can say then that the composition of a bond is going to be A subscript 1 over the coordination number of A, B, 1 over the coordination number of B.

The chemists abhor fractional subscripts on a chemical composition. So let's multiply this by the product of the two coordination numbers. And what we'll find is that the formula of the compound with integer subscripts is going to be A, C, and B; B coordination number of A. And that is a subject to a very drastic set of assumptions that each species A and B has just one coordination number.

OK, so doing this in terms of composition, just turning this result around. And then we'll quit and take a stretch. This says that if we look at a particular composition, A_nB_m , something like TiO_2 or Al_2O_3 , then the coordination number of A in proportion to the coordination number of B is going to be equal to the ratio of M to N.

And the more ions of one charge that we can pack around the other, the lower the energy will be. And, therefore, the coordination numbers will be the maximum permitted values of CNA and CNB, subject to the constraints of radius ratio.

In other words, to conclude very quickly with one specific example, if we look at a compound like Al_2O_3 , an important ceramic and a gemstone, this says that the coordination number of Al to the coordination number of the oxygen has to be equal to three to two. So possible structures might be aluminum with coordination number three, oxygen with coordination number equal to two. Or aluminum could have six coordination. The oxygen could have four coordination. Or the aluminum could have 12 coordination. And the oxygen could have eight coordination. Those three

possibilities.

Next we have to use the ionic sizes to see what constraints there are that are going to limit the maximum coordination numbers because the greater the number of neighbors, the lower the energy. And, in the case of aluminum oxide, it turns out that it's six to four. And this is determined by the radius ratio.

And you know what? If we used the ionic radii for Al^{3+} and O^{2-} , we were right one the nose. That is the nature of the structure of aluminum oxide-- aluminum with octahedral coordination by oxygen and oxygen with a tetrahedral coordination of aluminum. And that is the actual structure. The three-dimensional linkage would have to be such that ions of like charge have the maximum possible separation.

And to keep you beyond your patience for just a little bit, what is that going to be? We can use very simple considerations there. If we have coordination polyhedra and we want to join them together, the worst possible situation is to have them share edges because the central ions then had minimum separation.

The better situation would be to have to the polyhedra share corners and have the ions in the center of these triangles form a straight line with the shared ions. For a three-dimensional polyhedron, the sequence of increasing repulsive energy would be shared faces for something like cubes, shared edges-- that would be lower energy but not the best you could do. Shared corners would be the best possible arrangement.

As you make each of those transitions, you take the central ion and keep the separation between the neighboring ion of like charge as low as possible. The interaction energy would be as low as possible.

All right, so let me stop there. I think we're probably about halfway through. We can then determine ranges of radius ratio for various stoichiometries. And all this is just a fantasy unless we can say, do ions have sizes that are the same from compound to compound? And, if so, how do we determine them?

I hope that intriguing pair of questions will keep you here, dry and warm, rather than

heading off early. OK, so let's take our usual 10-minute break and resume to wrap this up.