Crystals, Symmetry and Tensors Professor Rajesh Prasad Department of Materials Science and Engineering, Indian Institute of Technology, Delhi Lecture 20 e 3D point Groups XIII: Chirality Revisited

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3D POINT GROUPS XIII Chirality Revisited Part V Chirality Chirality Enonhomerism Erantiomorphism Definition If an object and its mirror image cannot be superimposed by proper rotation then the object is said to exhibit chirality.

In part 5 of this series, we had discussed chirality and in this part we are going to revisit it looking at it little bit more detail. So, chirality also known as enantiomerism or enantiomorphism. So, these are all synonyms and sometimes in literature one also sees like a word like this dissymmetry all these are synonyms.

So, let us define chirality, if an object, object and its mirror image if an object and its mirror image cannot be superimposed that is cannot be brought into self-coincidence cannot be superimposed by proper rotation and the object is set to exhibit chirality or the object possesses chirality or it shows enantiomerism or enantiomorphism.

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E xampies > Not Chival A (Achiral) object image Schiral Z Dissymmetry Definition If an object and its mirror image cannot be superimposed by proper operation rotation then the object is said to exhibit chirality. Examples A. (¥) object image Definition If an object and its mirror image cannot be suberimposed by proper rotation, then the object is said to exhibit chirality. Examples > Not Chival (Achi object image

So, let us look at some examples some geometrical example simple example we will take. So, let us start with, with the English letter A. Now if I create a mirror image of this letter A so, I will get another A of this type. So, I can call this an object, this is an image and this is a mirror plane. Now, the image A can be superimposed on the object by a simple translation. If I translate this A you can see that I can superimpose on this.

Since translation now, I should maybe modify I should not say proper rotation because translation also I am using so I can say proper operation. So, can be a proper rotation or translation or I could have I could have emphasized rotation also maybe let me say write proper rotation or translation both are type 1 operation. So, essentially any type 1 operation.

If an object can be brought into self-coincidence with a type 1 operation in this case it can be brought into self-coincidence. For chirality the requirement wall that it cannot be brought cannot be superimposed.

So, since in this case it is being superimposed this is not chiral. Letter A is not chiral or I can say that this is A chiral. Now let us look at the last letter of the English alphabet the letter Z or before that let me do some more exercise.

Maybe, maybe you are thinking that since I used a vertical mirror I was able to superimpose what about if I use some other mirror let us say a horizontal mirror for the same way. If I use a horizontal mirror, then of course I will get the image which is an upside down nail.

But you can see that this upside down A by 180-degree rotation can be straightened up and then can be superimposed on they say by for the translation. So, it does not matter which mirror you use if the object is A chiral, its image will always be able to superimpose on the object by some proper operation of rotation or translation. But now, let me take the letter Z the last letter we took the first letter now we are taking the last letter of English alphabet.

If I now reflect this one in a mirror you can see that I get an inverted Z and now no rotation is possible which will bring this into self-coincidence with the original Z. Suppose if I rotate it by 90 degrees, if I rotate the image by 90 degree I get something like this.

So, a further 90 degree rotation you can see carefully it still brings it back to its image but it does not bring it to the object. So, no rotation is possible which will bring the image into coincidence with the object.

So, this object this Z is chiral so as per our definition this is chiral. If you see carefully Z has a 2 fold 2 fold symmetry. Whereas, if you look at A, A itself has a mirror plane as part of its symmetry.

So, this is giving us some hint regarding the symmetry requirement or symmetric condition for chirality which we will now write down.

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 $\sum \frac{40^{\circ}}{10^{\circ}} \sqrt{\frac{90}{10^{\circ}}} \sum_{\substack{\text{Chiral}\\\text{handed}}}$ Z Right handed Symmetry Condition for chirality $\frac{\text{Absence of any type II}}{\text{symmetry operation}} \Rightarrow \text{Chiral}$ $(\overline{I}, \overline{n}, \overline{n})$ Chiral Left-Right

Handed handed Symmetry Condition for chiralit Absence of any type II symmetry operation (I, m, T) Chiral Presence of any type II Oberation in the Symmetry of object ⇒ Achiral

Example Not Chival (Achiral) magé = Cannot have Right Kanded 3D POINT GROUPS XIII Chirality Revisited Part V : Chirality Enantiomorphism Enanhomerism Chirality Dissymmetr Definition If an object and its mirror image rotation, then the object is said to exhibit chirality

So, we can write the symmetry condition for chirality. Chirality as for chiral object we require absence of any type 2 symmetry operation. So, if the object symmetry does not have any type 2 operation type 2 operation as you know is roto-inversion of any kind so it can be inversion center or a mirrored plane or any roto- inverse in axis n bar.

So, this if these are absent, that is if the symmetry consists of only proper operations then the object will be chiral and it can show chirality it can come in two versions left-handed and right-handed version.

So, I can call this Z right handed Z, call this one as left handed. So, a chiral object can exist in two versions left and right so there is a proper Z and there is an inverted Z. Whereas, in A chiral object like A has only one form it cannot have handedness.

So, this cannot have handedness. So, the requirement for showing handedness requirement for showing chirality is that there should not be any type 2 operation in the object and the reverse of this is also true. So, the presence of any type 2 operation in the symmetry group this will imply that the object is A chiral.

So, this is the important symmetry distinction of the object showing chirality and object not showing chirality. The pair of object right-handed and left-handed pair this is what is called enantio enantiomers. So, if object is showing chirality the pair will be called either enantiomers or enantiomorphs both words are used. And that is why the effect also can either be called enantiomerism or enantiomorphism.

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Crystal System Chirol Groups Achiral Groups 1(C) 1 Triclinic 2 (C2) 2 Monaclinic $mm2(C_{22}), mmm(D_{2k})$ 3. Orthorhombic 222 (D,) 4, 422 4. Tetragonal 4mm, 4,420,4400 (G4 , D4) 12; Gahi Dats Dah) 5, Trigonal 3, 32 (C_{3}, D_{3}) (Cat, Can, Dad) 6 Hexagonal 6, 622 百, 6mm, 5/m, 62m,魚 mn (Co, D6) $m\bar{s}(T_a)$, $\bar{4}sm(T_a)$, msm(0)23(7), 432(0) Gubic

Crystal System 1 Triclinic	Chiral Group: 1 (C ₁)	Achiral Graups
2 Monaclinic	2 (C2)	
3. Orthorhombio 4. Tetragonal 5. Trigonal	4, 422 (G4, D4) 3, 32	$\begin{array}{c} mm2(C_{29}), mmm(P_{2h})\\ \overline{i}, 4mm, \frac{4}{m}, \overline{4}2m, \frac{4}{m}m\\ (S_q, C_{qy}, C_{qh}, D_{2d}, D_{qh})\\ \overline{3}, 3m, \overline{3}m \end{array}$
6 Hexogenal ∰ 7 Сиріс	(C_3, D_3) $(C_6, 622)$ (C_6, D_6) 25(T), 432(0)	(C3t、C32t、D3d) る、GMM、G/10、G2m、Gmmm (C55、C65t、C66t、D355、D66) かま(Tp)、F3m(Tp)、M3m(Q)

Now, once we have established that it is easy to see which point groups will show chirality and which cannot show. So, since the chiral groups should not have any type 2 operation they should have only proper rotations and we have already established this we have shown that there are 11 such groups. Here I have shown you divided by crystal system.

So, there are 11 such groups which have only proper rotations the 5 monoaxial groups 1,2,3,4 and 6 and 4 dihedral groups 222, 422, 32 and 622 and 2 cubic groups 23 and 432 only these 11 crystals having only these 11 point groups shown in red here can show chirality can occur in both left-handed and right-handed versions. If you have symmetry of these other group shown in blue here these other 21 point groups.

These cannot show handedness cannot show chirality because all of them as you can see have some type 2 operation like a mirror or inversion center or a roto inversion axis.

ofical Activity and Chinality Robotton of plane of polarization of light. > Only chiral crystals (i.e crystals with chinal point groups can show optical activity)

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Let me end this discussion with an interesting effect which is shown by chiral molecules can be shown by chiral molecules is Optical activity. So, Optical activity as you know is rotation of plane of polarization of light by a material.

If the material can as the light passes through a material if the plane of polarization rotates we say that the material is optically active. Now, optically active material have to have one of the chiral point groups. A chiral point group materials cannot show Optical activity. So, Optical activity and chirality are related only chiral crystals that is crystals with chiral point groups can show Optical activity.

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L. Posteur 1849 Tartoric Acid (Cg. Hg. Og.) derived from Chemical organic source, Synthusis nowed optical Did not show activity optical activity derived from (snowed optical L. Pasteur 1849 Tartaric Acid (C4 H6 06) derived from Chemical organic source Synthesis showed optical Did not show activity Optical activity (one handedness) (mixture of L and

Interesting history historical fact regarding this Optical activity is the discovery by Louis Pasteur, who in 1849 several years ago about 170 years ago. In 1849 he solved a big conundrum a big puzzle of that time.

And the puzzle was that people were studying, studying Tartaric acid C4 H6 O6 and it was found that a Tartaric acid derived from organic source organic source showed Optical activity. But this exactly same composition Tartaric acid synthesized in laboratory that is by chemical synthesis did not show Optical activity.

So, this was a big question of that time, that why the same compound derived from different sources by organic source and biochemical synthesis is showing this different behaviour. One is optically active another is not optically active and Pasteur in a beautiful set of experiments could show that the crystals derived from the organic source were all of one-handedness. Whereas, those derived from chemical synthesis were mixture equal mixture equi mixture of left and right-handed crystals.

So, he actually crystallized these compounds and manually in 1849 manually separated the left-handed and right-handed crystals from the compound and then could show that because of the mixture equal mixture of left-handed and right-handed although individually they are capable of rotating the plane of polarization but when you mix them in equal amounts they will they cancel the Optical activity of each other and there is no net Optical activity shown by the compound. So, chirality is related to this Optical phenomenon and Pasteur is remembered for this very important contribution to science. Thank you very much.