Solid State Physics
Lecture 60
Crystal Field Splitting

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We move on to Crystal Field Splitting, this is something very interesting and it is very important for the idea of magnetism. The difference in behavior of rare earth and transition metal is that 4f shells responsible for paramagnetism or ferromagnetism in or antiferromagnetism in rare earth ions that lie deep inside the ions; that means, 4f shells are covered by 5s and 5p states. While 3d orbital's that are responsible in transition metals 3d transition metals. They are kind of outermost shell because if you consider ions of the transition metals the s electrons are given away, the positive ions of transition metals have S electrons given away. So, 3d becomes the outermost shell in that case. And therefore, it has a strong dependence on the crystal field on how the magnetic properties behave. (Refer Slide Time: 01:51)

Let us see in pictures to understand how these things work. If we consider isolated atom then it does not have any it is not in a crystal. So, therefore, there is no question of a crystal field in that kind of an atom so it has many degenerate orbital's, for example if there are three p orbitals all those p orbitals are degenerate. Let us consider 3d orbital's those are most interesting in our case there are 5 3d orbital's all those d orbital's are degenerate; that means, all those are at equal energy level. However, if we consider an atom in a crystal the situation becomes different; the atom is coordinated by few other atoms. And depending on the crystal the coordination style of the coordination differs. If we consider high symmetry crystal like cubic crystals, mostly there are two different kinds of coordination's one is octahedral that forms an octahedral after the octahedron after the coordination it has 6 neighbors and the other one is tetrahedral it forms a tetrahedron keeping the ion of interest atom of interest at the center of the tetrahedron with 4 neighbors. (Refer Slide Time: 03:14)

So, here is one example of octahedron code octahedral coordination the center atom the pink one that is our 3d transition metal ion of interest and these white atoms are the coordinate coordinating atom atoms. So, you can see that there are 6 white atoms this makes an octahedron keeping the transition metal atom at the center and if we look at the energies of the 3d orbital's here we can see that xy, yz and zx they have lower and equal energy so these are three fold degenerate. On the other hand, z^2 and $x^2 - y^2$ they have higher energy and these two are also degenerate. So, these three orbitals are called t_{2g} orbitals these two orbital's are called e_g orbitals t_{2g} are lower in energy e_g are higher in energy, why is it so? (Refer Slide Time: 04:20)

Because if you look at the orbital shapes xy yz and zx they have this kind of a shape they do not point towards x-axis or y-axis or z-axis, they are lying in between x and y-axis. And these ligands these directions are x-axis, y-axis and z-axis. So, these three orbital's are not pointing towards any atom in the surrounding Therefore, they have a lower energy because the coulomb interaction is not that effective in this; however, if we consider e_g orbitals these orbitals are pointing along this this and these orbitals z^2 they are pointing along these atoms. Therefore coulomb interaction is stronger and because of that coulomb repulsion they have higher energy in case of octahedral coordination. Now, if we look at a tetrahedral coordination this is the picture here the situation completely reverses, we have e_g with lower energy and t_{2g} with higher energy, but the splitting is still e_g and t_{2g} and the splitting could be different if the crystal field is different. So, there are many different possibilities for crystal fields in many different crystals, this is for higher symmetric crystals cubic crystals that this kind of crystal fields are realized also apart from cubic crystals these crystal fields are realized. So, we will now see, what is the consequence of this kind of crystal field splitting of the otherwise degenerate states on magnetism? (Refer Slide Time: 06:17)

So, they have quite serious implication on magnetism if we consider an octahedral crystal field t_{2g} is lower and e_g is higher in energy and if we consider very strong crystal field that is this gap between t_{2g} and e_g is pretty large then we will have up spin and down spin electrons. So, if we have 5 electrons in the d shell we will have 2 of the t_{2g} orbitals occupied by up spin and downspin electrons that is fully occupied and one is partially occupied while e_g will be completely empty. And this will give us how much of spin this will give us 0 from here 0 from here and $\frac{1}{2}$ from here. So, this is a low spin configuration for this kind of a system because we have a very large crystal fields field splitting. As opposed to that if we consider a weak crystal field a small crystal field splitting then we can have all the orbital's all the 5 orbitals that we can see here partially occupied. And if we have all the 5 orbitals partially occupied clearly it leads to a high spin configuration where the magnetic moment coming from this atom would be much larger. Therefore, you can see that the crystal field effect has quite strong consequence on the magnetic properties of a material and also Hund's coupling strength matters Hund's coupling strength tells you the energy difference that should appear between doubly occupied and partially. So, up spin and down spin electron the splitting of up spin and down spin electron comes from the Hund's coupling strength. So, an inter play between crystal field strength and Hund's coupling strength that suggests whether a low spin configuration would be realized or a high spin configuration would be realized. And in many different kind of crystal fields with many different number of electrons in the 3d orbital's the consequences could be very different. So, this is about crystal field effect in crystals.