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Digital Computer Laboratory
Massachusetts Institute of Technology
Cambridge, Massachusetts

SUBJECT: GROUP 63 SEMINAR ON MAGNETISM, XXXVIII

To: Group 63 Engineers

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At the previous meeting the phenomenon of double exchange was discussed. This type of interaction was between two degenerate systems in the ground system, and was found to lead to ferromagnetism and electrical conductivity.

Another phenomenon involving coupling of transition atoms through an intermediate atom is called superexchange, which should not be confused with double exchange. In order to explain the phenomenon of superexchange, consider a chain of atoms of the form

where B is a doubly negative charged ion with a closed p shell (e.g., oxygen, sulfur). The A atoms are transition elements.

In superexchange we consider the possibility of coupling arising from a mixture of the ground state with excited states (states in which the B atom gives a p electron to the A atom.) If the energy of the excited state is low enough to be near that of the ground state, there will be a great deal of admixture. This arises from the fact, discussed at meeting 25, that the amount of admixture is greatest between states of small energy difference and large coupling.

That is, the amount of admixture is proportional to

$$\frac{H'_{nk}}{H_{kk} - H_{nn}}$$

The factor H'_{nk} represents the coupling between the n^{th} and k^{th} states and is equal to

$$\int \psi^*_n H' \psi_k \, d\tau,$$

and in this case H' is of the form $\frac{e^2}{r}$. Thus

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$$H'_{nk} = \int \psi_n^* \frac{e^2}{r_{nk}} \psi_k \, d\tau$$

where r_{nk} is a separation of the electrons corresponding to the n^{th} and k^{th} levels. If the overlap of the n^{th} and k^{th} states is small, as indicated in figure 67 a, the exchange interaction will be slight since the product of ψ_n and ψ_k is small everywhere. If the functions are moved closer together, as in figure 67 b, there can be considerable overlap, and in this region of overlap the product of ψ_k and ψ_n increases accordingly.

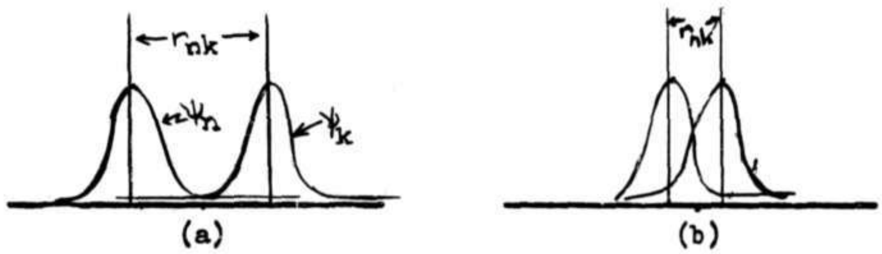


FIGURE 67

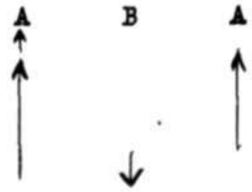
On examining the possible excited states, two criteria should be used to determine which of the excited states is in the lowest energy state. They are:

1. Hund's rule: This rule states that the electron spins in an unfilled shell tends to be aligned so as to yield the maximum total spin consistent with the number of electrons in the shell and the Pauli exclusion principle. Therefore, if the 3d shell of atom A is less than half full, the additional electron will tend to align itself parallel with the resultant spin. On the other hand, if the 3d shell is half occupied or more than half occupied, the exclusion principle requires that the additional electron align itself anti-parallel to the existing net spin in the d shell.

2. The exchange effect: According to this effect the remaining spin of the B atom in the excited state tends to be aligned anti-parallel to that of the neighboring A atom.

On the basis of the above criteria, let us consider which of the four possible excited states will have the lowest energy for the case in which the 3d electron is less than half full.

1. A B A



with Hund's rule
with exchange energy

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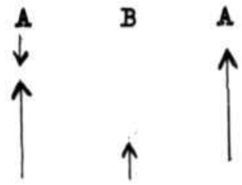
2.

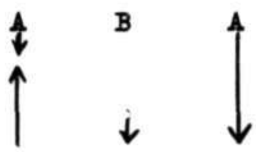


against Hund's rule
against exchange energy

3.

with Hund's rule
partially against exchange energy

4.

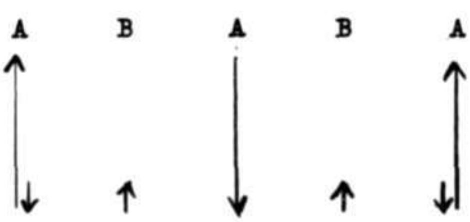


against Hund's rule
partially against exchange energy

Thus of the four possibilities listed above, the first case is the one with the lowest energy and thus involves the greatest admixing. Since the transition atoms in this case are aligned parallel, we obtain ferromagnetism with the d shell < half full. Furthermore, this model permits electron migration, so the material should be a good conductor.

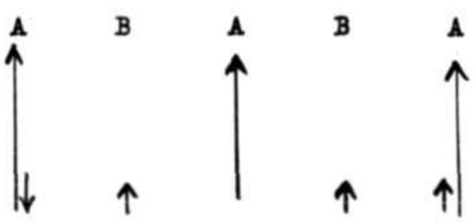
For d ≥ half full an analysis similar to the above can be made. Since one half shell is full, in accordance with Hund's rule, the exclusion principle requires that the electron of the B atom transferred to the A atom have its spin aligned anti-parallel to the resultant spin of the d shell of atom A. Therefore, in our analysis for the case d ≥ half full, we can eliminate cases 2 and 4 of the previous analysis as violating the exclusion principle. Then, we have the two remaining possibilities:

1.



partially against exchange energy

2.



totally against exchange energy

Thus the first case above is the most stable, so for d ≥ half full we have anti-ferromagnetism and poor conductivity.

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In considering the interaction of the A and B atoms one must take into account the fact that the wave function of the B atom, which has a closed p shell, has a dumb-bell like shape as shown in figure 68.

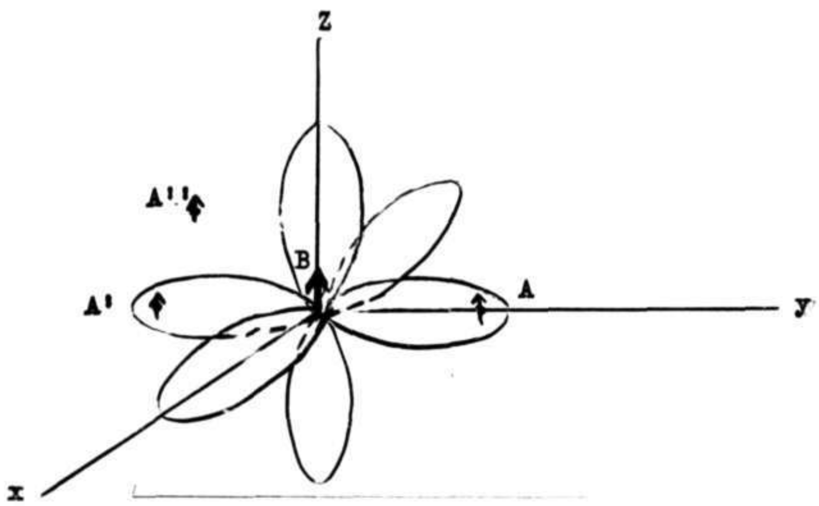

FIGURE 68

Thus atom A will react more strongly with atom A', located as shown in figure 68, than it will with atom A''. This effect introduces a strong angular dependence.

Zener correlates conductivity and ferromagnetism, but in the ferrites we find a material of high magnetization and poor conductivity. This apparent contradiction arises from the fact that ferrites are ferrimagnetic rather than ferromagnetic. That is, there are two distinct types of lattice sites present in the crystal. They are the octahedral sites (with six oxygen neighbors) and tetrahedral sites (with four oxygen neighbors). There are twice as many octahedral sites in the crystal as tetrahedral.

The ferrites have the composition $M^{+2}O^{-2}$ Fe_2^{+3} O_3^{-2}, where M represents a metal or mixture of metals (eg. N^{++}, Zn^{++}, Fe^{++} etc.). In a normal spinel structure all the Fe^{+++} ions are located in the octahedral sites with anti-parallel alignment, while the M^{++} ions are in the tetrahedral sites. This arrangement leads to anti-ferromagnetism. In the inverse spinel structure half the octahedral sites and all the tetrahedral sites are occupied by Fe^{+++} ions, and the remaining octahedral sites are occupied by M^{++} ions, The Fe^{+++} ions in the octahedral and tetrahedral sites are aligned anti-parallel to each other. However, ferromagnetic M^{++} ions are aligned parallel to the Fe^{+++} ions in the other octahedral sites and high magnetization results. If the M^{++} ion is not ferromagnetic, the only possibility of obtaining a material with a high magnetization is that there be a mixture of normal and inverse spinel structure, i.e. that the M^{++} ions be on both octahedral and tetrahedral sites. $Zn\,O\,Fe_2O_3$ is a normal spinel and has no magnetization. $Mg\,O\,Fe_2O_3$ is reported to be a mixed spinel. It has

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high magnetization.

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