

Memorandum M-1910

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SUBJECT: GROUP 63 SEMINAR ON MAGNETISM, XXXVII

To: Group 63 Engineers

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Date: March 13, 1953

On the basis of his ferromagnetic model, Zener discusses the correlation between conductivity and ferromagnetism found experimentally by Jonker and Van Santen*† with perovskite. Perovskite has the structure shown in figure 66 and has the composition $(La_{1-x}A_x)MnO_3$. A represents Ca, Sr, or Ba, while x is a measure of the relative density of La and A, varying from 0 to 1.

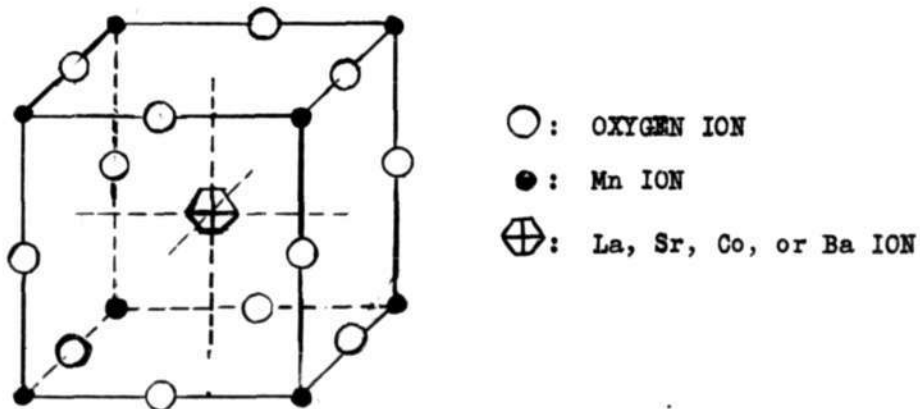


FIGURE 66

The compound $LaMnO_3$ has the ionic composition $La^{+3}Mn^{+3}O_3^{-2}$. However, Ca, Sr, and Ba have only two electrons outside a closed shell. Since the oxygen atoms have a strong affinity for two electrons, replacing La^{+3} by Ca^{+2} , Sr^{+2} , or Ba^{+2} results in a corresponding number of Mn^{+3} atoms becoming Mn^{+4} .

Compounds of the extreme values ($x=0$ or 1) were found to be poor conductors and were not ferromagnetic. For intermediate values of x , specifically $0.2 < x < 0.4$ the ferromagnetism and conductivity had their maximum value. The electrical conductivity is good only within this range of values of x , decreasing by a factor of .01 as x is increased to 0.6 or decreased to 0.1.

* G. H. Jonker and J. H. Van Santen, *Physica* 16, 337, (1950)

† J. H. Van Santen and G. H. Jonker, *Physica* 16, 599, (1950)

Zener examines this problem from the point of view of the double well. Since the Mn^{+3} and Mn^{+4} atoms are in equivalent sites one would expect some type of resonance between them. This is due to an additional electron in the Mn^{+3} compared to the Mn^{+4} ion.

Since the manganese ions are relatively far apart, any transfer of this electron takes place through oxygen ions. Thus we denote the wave functions ψ_1 and ψ_2 for the different positions of the extra electron as follows:

$$\psi_1^0 = Mn^{+3} O^{-2} Mn^{+4}$$

$$\psi_2^0 = Mn^{+4} O^{-2} Mn^{+3}$$

Zener calls this exchange through the oxygen a double exchange. Physically, this means that the electron of the Mn^{+3} ion migrates to a neighboring oxygen ion. The oxygen ion then has more electrons than the exclusion principle allows without going into a higher energy shell, so an electron with the same spin can then leave the O^{-2} ion toward the Mn^{+4} ion.

The functions ψ_1^0 and ψ_2^0 are degenerate, and linear combinations must be used as the stationary perturbed states. The lowest energy of the system is that corresponding to a parallel spin alignment of the Mn d shells, thus leading to ferromagnetism. The double exchange also leads to electrical conductivity because the exchange energy lowers the barrier allowing electrons to migrate through the crystal.

A quantitative relationship between ferromagnetism and electrical conductivity must now be established. The Einstein relation gives

$$\sigma = \frac{ne^2 a^2 \epsilon}{h k T}$$

wherein n = no. of Mn^{+4} ions per unit volume

e = electron charge

a = lattice parameter

ϵ = exchange energy

h = Planck's constant

k = Boltzmann constant

T = temperature

Therefore

$$\sigma = \frac{x e^2 \epsilon}{a h k T}$$

where x = fraction of Mn ions with +4 charge.

Since ferromagnetism disappears at the Curie point, the Curie temperature T_c is approximately given by

$$kT_c \sim E$$

Therefore

$$\sigma \approx \frac{xe^2 T_c}{ah T}$$

XXXVII-1

This expression gives quantitative agreement with the experimental results of Jonker and Van Santan.

In his third paper of his series on ferromagnetism, Zener undertakes a quantitative analysis based on his model.

According to the original Weiss theory

$$H_{\text{eff}} = H + WJ$$

where H_{eff} = effective magnetic field
 H = applied magnetic field
 J = magnetization intensity
 W = constant of proportionality called the Weiss factor.

The energy of interaction is then

$$\begin{aligned} E_{\text{spin}} &= -\frac{1}{2} WJ^2 \text{ per cm}^2 \\ &= -\frac{1}{2} W' S_d^2 \text{ per atom} \end{aligned}$$

XXXVII-2

where $W' = N \mu_B^2 W$

and μ_B = Bohr magneton
 N = no. of atoms/unit volume

Comparing XXXVII-2 with XXXVII-3 we see

$$W' = \frac{E^2}{J} - \alpha$$

XXXVII-3

These terms were defined at the previous meeting, where we found

$$E_{\text{spin}} = \frac{1}{2} \alpha S_d^2 - \beta S_c S_d + \frac{1}{2} \gamma S_c^2 \quad \text{XXXVI-1}$$

The coefficient α is proportional to the direct d-d exchange coupling, and in ferromagnetic materials it is smaller than β^2 . Since there is no apparent means of calculating α , it will be neglected. γ This gives us an upper limit for W' .

We may determine β from spectroscopic data for the following reason. If we have a d shell with spin oriented up (\uparrow), the conduction electrons may have spin oriented up (\uparrow) or down (\downarrow). The parallel alignment leads to a lower energy because of the exchange effect, and a measure of this energy difference in isolated atoms (gas) can be determined from spectroscopic data.

Let us consider the iron atom. This has the configuration $3d^6 4s^2$ and becomes $3d^7 4s$ with the demotion of a conduction electron. This may be written as a $3d^7 ({}^4F) 4s$ state, where the F corresponds to $\sum m_l$ of the total d band equal to 3, and the preceding superscript 4 corresponds to the multiplicity. (quadruplet.)

This is arrived at in the following way. The seven electrons in the 3d shell will have the following spin and angular momentum components:

<u>M_l</u>	<u>M_s</u>
2	+ 1/2
1	+ 1/2
0	+ 1/2
-1	+ 1/2
-2	+ 1/2
2	- 1/2
1	- 1/2
$\sum M_l = 3$	$\sum M_s = 3/2$

The unbalanced angular orbital momentum will therefore be 3 (F), and the unbalance spin can be 3/2, 1/2, -1/2, -3/2, leading to a 4-fold multiplicity.

If a 4s electron ($M_l = 0$, $s = + 1/2$) is added to the seven 3d electrons we have a 3F or 5F state depending upon the spin orientation of the 4s electron. The 5F state lies 0.624 electron volts lower than the 3F state.

This difference arises from the fact that for the conduction electron oriented to have spin $+1/2$, exchange interaction will take place between the conduction electron and five d electrons, whereas if the spin direction is $-1/2$, this interaction will take place between the conduction electron and only two d electrons. Since each electron involved in the coupling term contributes one-half to S_d , and S_c equals one-half we have, for the difference in the exchange coupling energies $C(\beta S_c S_d)$

$$\beta \times \frac{1}{2} \times 5 - \beta \times \frac{1}{2} \times 1 = \frac{3\beta}{4} = 0.624$$

Therefore

$$\beta = \frac{4 \times 0.624}{3} \text{ per atom}$$

Since there are eight electrons involved in the coupling, we divide the above by eight to obtain the value of the coefficient β per electron.

This yields

$$\beta_0 = 0.104 \text{ ev. per electron}$$

In the solid state the conduction electrons are in the region of a d shell 3.28 times as often as in a gaseous state. Therefore

$$\frac{\beta}{\beta_0} = 3.28$$

$$\beta = 3.41 \text{ ev.}$$

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As was shown at meeting XXXIII, the two factors contributing to γ are the Fermi energy and the exchange energy. Assuming freely moving conduction electrons the Fermi energy gives rise to the positive contribution

$$\gamma_{KE} = \left(\frac{10}{9}\right) \frac{\bar{\epsilon}_k}{v}$$

and the exchange energy gives the negative contribution

$$\gamma_{ex} = \left(\frac{4}{9}\right) \frac{\bar{\epsilon}_{ex}}{v}$$

where $\bar{\epsilon}_k = 21.82 n^{2/3}$ ev. = average Fermi energy
 $\bar{\epsilon}_{ex} = 10.81 n^{1/3}$ ev. = exchange energy per conduction electron
 v = number of conduction electrons per atom
 n = number of conduction electrons per unit volume

Therefore,

$$\gamma = \gamma_{ke} - \gamma_{ex} = 21.82 \left(\frac{10}{9}\right) \frac{n^{2/3}}{v} - 10.81 \left(\frac{4}{9}\right) \frac{n^{1/3}}{v}$$

The correlation between this and the final equation of meeting XXXIII, namely

$$E = A \left(\frac{N}{v}\right)^{2/3} - B \left(\frac{N}{v}\right)^{1/3}$$

is at once apparent. The coefficients $\left(\frac{10}{9}\right)$ and $\left(\frac{4}{9}\right)$ arise from an expansion, as was shown in meeting XXXIV (equation XXXIV - 2).

Essentially the difference between Bloch's collective and Zener's atomistic approach can be described as follows: Bloch's calculations for freely moving electrons did not produce correct magnitude for A and B. Bloch then replaced his freely moving electrons by electrons moving in a periodic field, so that lower energy electrons experience considerable resistance to motion. Zener divides his electrons into two groups: freely moving s electrons, and d electrons that are localized.

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