Digital Computer Laboratory
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SUBJECT: GROUP 63 SEMINAR ON MAGNETISM, XXXV

To: Group 63 Staff

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This seminar on magnetism, conceived as an introduction to the generally accepted fundamental aspects of ferromagnetism, came to a close at the previous meeting. The meetings will continue with consideration of various recent publications in this field and of fundamental research done in our own group.

We will first discuss the Zener model of ferromagnetism as set forth in a series of articles.*

Zener was led to his theory as a consequence of his study of crystal structure. In order to better understand his work, a brief introduction of the effect of crystal structure on the electron spins in a material will be given.

Let us consider the carbon atom, of atomic number 6. In the ground state one would then expect to find two 1s electrons, two 2s electrons, and two 2p electrons. The situation here is similar to that of the double well problem, which was considered at meeting 24. We then found that if the wave function corresponding to the electron being in well 1 is given by ψ_1^o, and the function corresponding to electron in well 2 is ψ_2^o, the electron oscillated between the wells and stationary states given by

$$\frac{1}{\sqrt{2}} (\psi_1^o \pm \psi_2^o).$$

For carbon, we have a comparable situation in that interactions will occur amongst the 2s and 2p electrons. The perturbations due to electrostatic interactions between electrons gives rise to stationary states made up of a mixture of the unperturbed 2s and 2p states. The stationary state with lowest energy is one with all four spins parallel. The electronic space distribution is as shown in figure 61(a) with the average distance between the four electrons as large as possible in accordance with Pauli's exclusion principle.

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* C. Zener, "Interaction Between the d Shells in the Transition Metals,"
    I, II, III, IV, Physical Review, 81, 82, 83, 1951; 85, 1952.

FIGURE 61

     If a second carbon atom joined the first, it would have electrons
with spins anti-parallel to those of the first. This is because no more than
four symmetric space states are available; additional electrons must there-
fore fill the already occupied states with extra spins. Thus antiparallel elec-
tron pairs are formed. These are chemical valence bonds. Mixing unperturbed s
and p states to form stationary perturbed states is called hybridization by chem-
ists. **Figure** 61 (b) **shows the two atoms with a single bond.**
The shaded regions represent the regions of electron distribution, and the
net spin in the region common to both atoms is zero. As more carbon atoms
are formed, all the regions would contain electrons of anti-parallel spin.
The resultant crystal would then be a very poor conductor as all the holes
are filled. We see from the above that the orbitals are not just a random
cloud, but that certain directions are more probable than others.

     The tetrahedral lattice discussed above is the diamond structure.
However, carbon also exists in a different lattice form, and is then known
as graphite. The lattice structure of graphite is hexagonal and planar; a
representation is shown in figure 62. Each carbon atom contributes three
2p electrons to the lattice structure, leaving a 2s electron to act as s
conduction electron. For this reason, graphite has a relatively high elec-
trical conductivity and has metallic lustre. Forces are strong within planes
as shown in fig. 62, but weak between different planes. Therefore planes
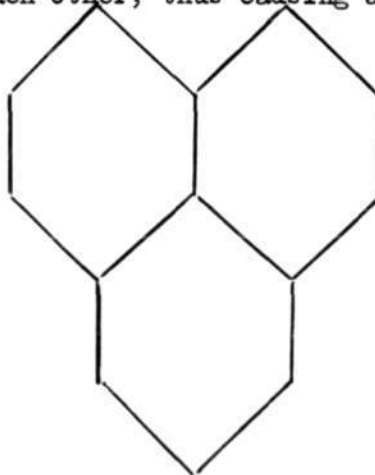easily slide over each other, thus causing a slippery feel.

FIGURE 62

TABLE I: Isolated Atoms

ELEMENT	V	Cr	Mn	Fe	Co	Ni
ATOMIC NUMBER	23	24	25	26	27	28
ELECTRON DISTRIBUTION	$3d^3 4s^2$	$3d^5 4s^1$	$3d^5 4s^2$	$3d^6 4s^2$	$3d^7 4s^2$	$3d^8 4s^2$
CRYSTAL STRUCTURE	bcc	bcc	complex	fcc bcc	hcp	fcc

ELEMENT	Cb	Mo	Ma	Ru	Rh	Pd
ATOMIC NUMBER	41	42	43	44	45	46
ELECTRON DISTRIBUTION	$4d^4 5s^1$	$4d^5 5s^1$	$4d^6 5s^1$	$4d^7 5s^1$	$4d^8 5s^1$	$4d^{10}$
CRYSTAL STRUCTURE	bcc	bcc	unknown	hcp	fcc	fcc

ELEMENT	Ta	W	Re	Os	Ir	Pt
ATOMIC NUMBER	73	74	75	76	77	78
ELECTRON DISTRIBUTION	$5d^3 6s^2$	$5d^4 6s^2$	$5d^5 6s^2$	$5d^6 6s^2$	$5d^7 6s^2$	$5d^9 6s^1$
CRYSTAL STRUCTURE	bcc	bcc	hcp	hcp	fcc	fcc

note: bcc = body-centered cubic

fcc = face-centered cubic

hcp = hexagonal close packed

Zener bases his theory on 3 basic principles. These are:

1. In the fourth column of the periodic table (V, Cb, Ta) and beyond, the spin correlation between electrons in the incomplete d shell of an atom is the same whether the atom is in a crystal or in gaseous state. Thus, according to this principle the net electron spin in the incomplete d shell is the highest value consistent with the total number of electrons in the shell.

2. The exchange integral between d shells of adjacent atoms always has the same sign as in the H_2 molecule.

3. The spin of an incomplete d shell is strongly coupled to the spin of the conduction electrons.

Let us now examine the physical significance of the above principles in terms of a particular atom with a $3d^5$ outer shell. In accordance with Zener's first principle all five 3d electrons will tend to line up with their spins parallel. According to the exclusion principle, only 5 electrons can exist in the 3d shell with the same spin direction ($M\ell$ = 2, 1, 0, -1, -2), so the space states with this spin orientation are all filled.

On bringing a second atom close to the first, the exchange interaction of the incomplete d shells will tend to align the spins of the neighboring shells anti-parallel since all space states with the same spin function have been filled. Therefore there is a strong tendency toward anti-ferromagnetism. This effect is stronger for larger net d shell spins, so it will be strongest for the case in which there are five 3d electrons.

At this point it should be noted that the first two principles alone can never account for ferromagnetism. According to the Slater model, the exchange interaction is assumed to change sign, and as we have seen, ferromagnetism occurs only when this integral is negative. Since Zener makes no assumption of a sign change, another mechanism must be used to account for ferromagnetism. This mechanism is the strong coupling of the d shell electrons and the conduction (s) electrons.

Since 4s and 3d electrons have about the same energy the outer s shell is always coupled fairly strongly to the incomplete d shell in isolated atoms. The energy is always lowest for the spin of the s shell parallel to that of the d shell.

Let us assume that the $3d^5$ atom we have chosen also has a 4s electron ($3d^5 4s^1$). When another atom is brought near the first one the d shell of the second electron will tend to align itself anti-parallel to the d shell of the first electron for the reason previously noted. The s electrons are free to move from atom to atom but its spin direction is taken as invariant. Since the s electrons have this mobility they will alternately encounter d shells with spin parallel and anti-parallel to their own spin. This configuration involves a higher average energy than would exist if all the d spins were aligned parallel. Thus s-d coupling favors parallel alignment of the d-spins. If this latter tendency prevails over the direct anti-parallel d shell coupling, the material is ferromagnetic.

In the particular example we have chosen $(3d^5 4s^1)$ the d-d exchange interaction is very strong, and this configuration would be expected to lead to anti-ferromagnetism.

When atoms are in a condensed system there is a broadening of bands, and the energy required for electrons to remain in the 4s shell will increase. Therefore there will be a tendency for some of the 4s electrons to be demoted to the inner 3d shell.

In general, this leads to one or less 4s electrons per atom in the outer shell, and explains such seemingly odd results as finding that nickel has 0.6 4s electrons per atom. This is an average value and means that of the ten 4s electrons originally associated with 5 nickel atoms, seven have been demoted to the inner 3d shell.

If one assumes that one electron or less remains in the conduction electron after demotion, we see from Table I that chromium, molybdenum, and tungsten will have the most unpaired electrons in the d shell. Since this gives the greatest d shell spin, these elements will have the greatest tendency to form a lattice structure in which all nearest neighbors have anti-parallel spin. While neither face-centered or hexagonal close packed lattices can be arranged so that all neighboring atoms have opposite spins, this arrangement can be obtained in a body-centered lattice, as shown in figure 63. The stable configuration of these three elements is the body-centered lattice, in agreement with this hypothesis
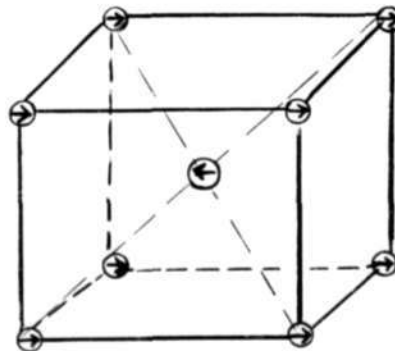

FIGURE 63

Next to chromium, molybdenum, and tungsten, the elements with the most unpaired d electrons are vanadium, columbium, and tantalum. From Table I, one can see that these elements also exist in a body-centered lattice. Furthermore, these six are the only transition elements which are stable only in the body-centered lattice.

On the basis of this model, Zener is able to explain the ferromagnetism of the Heusler alloys, which contain manganese, copper, and aluminum. None of these elements is ferromagnetic but one of them, manganese, is a transition element. In the alloy the manganese atoms are in positions which are next nearest neighbors of one another, and are 40% farther apart than in pure manganese. As a result, the exchange interaction between the manganese atoms

is much smaller than it would be in pure manganese, so the conduction electron coupling can produce ferromagnetism.

A large separation between atoms with $\underline{d}$ shells produces ferromagnetism only when there are conduction electrons present to provide ferromagnetic coupling. Thus, although the neighboring manganese atoms in $MnCl_2$ are also 40% further apart than they are in pure manganese, $MnCl_2$ is anti-ferromagnetic because it contains no conduction electrons.

Signed _____
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