

Memorandum M-1918

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

To: Group 63 Engineers

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According to the Zener model, iron is ferrimagnetic and exists as a body centered ionic crystal. Energy is required to charge the system. The work required to remove a charge q from an isolated sphere of radius R is $\frac{q^2}{2R}$ (figure 71 a), and applying this charge to another similar sphere requires a like amount of work, for the energy is proportional to q^2 , hence independent of the sign of the charge. However, if the oppositely charged sphere is brought near the first sphere, some work is liberated by the system due to the electrostatic attraction (figure 71 b). In a body centered lattice structure the work done by the system is $\frac{1.76 q^2}{D}$.

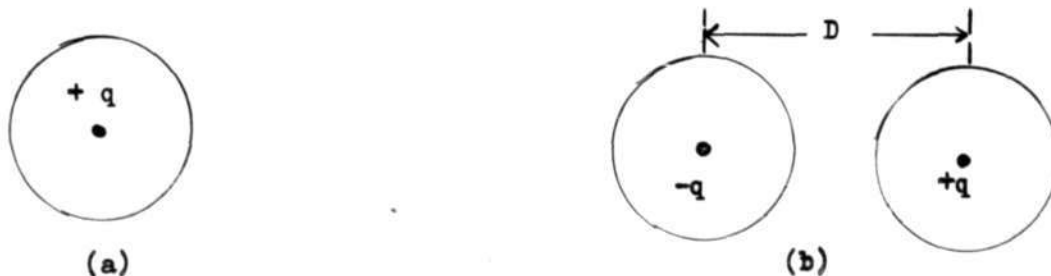


FIGURE 71

In a close packed lattice $D = 2R$, so the total work done in charging the system is

$$\frac{q^2}{R} - \frac{1.76 q^2}{2R} = \frac{0.12 q^2}{R} = \text{Madelung Energy}$$

XL-1

If, as explained at the previous meeting, the resonance energy for four pairs of electrons is great enough to overcome the Madelung energy, the ionic body-centered ferrimagnetic arrangement will be the stable one for iron.

Zener next discusses the magnetic structures of iron alloyed with other first row transition metals in a body centered structure. The variation of the saturation magnetization of these alloys can be approximated by

$$\frac{d\mu}{dN} = \mu_B$$

XL-2

where μ is the saturation magnetic moment per atom, N is the number of electrons of the alloying element, and μ_B represents a Bohr magneton. When the average magnetic moment has reached $5 \mu_B$, further additions reverse the sign of $\frac{d\mu}{dN}$. The reason for this will be shown later.

Table I shows the spin orientation and the number of exchange pairs of the 3d electrons of the first row transition elements in the solid state.

TABLE I

<u>Element</u>	<u>Atomic No.</u>	<u>Spin Orientation</u>	<u>No. Pairs</u>
Vanadium	23	→ → → →	6
Chromium	24	→ → → → →	10
Manganese	25	→ → → → ↺	10
Iron	26	→ → → ↺ ↺	11
Cobalt	27	→ → ↺ ↺ ↺	13
Nickel	28	→ ↺ ↺ ↺ ↺	16

Upon combination with iron as an alloying element, there will be a tendency for the d shell electrons of the iron atom and the neighboring alloying atom to redistribute themselves so as to reduce the energy to a minimum. Since the exchange interaction introduces a negative energy factor, the spins should align themselves so as to maximize the number of exchange pairs. This exchange effect will dominate if the exchange energy is greater than the Madelung energy. From this point of view let us consider the spin alignment one might expect for the various alloys. The results are shown in Table II.

TABLE II

Alloy	Spin alignment		μ	No. Pairs	
	Atom 1	Atom 2		Alloy	Individual Atoms
Fe V	$\rightarrow \rightarrow \rightarrow \rightarrow \rightarrow$ \uparrow Fe ⁺ V ⁼	$\leftarrow \leftarrow \leftarrow \leftarrow \leftarrow$ \downarrow Fe ⁺⁺	$4\mu_B$	20	17
Fe Cr	$\rightarrow \rightarrow \rightarrow \rightarrow \rightarrow$ $\uparrow \uparrow$ Fe Cr ⁼	$\leftarrow \leftarrow \leftarrow \leftarrow \leftarrow$ Cr Fe ⁺⁺	$2\mu_B$	21	21
Fe Mn	$\rightarrow \rightarrow \rightarrow \rightarrow \rightarrow$ $\leftarrow \leftarrow \leftarrow$ Fe ⁻ Mn ⁼	$\leftarrow \leftarrow \leftarrow \leftarrow \leftarrow$ Mn ⁺ Fe ⁺⁺	$3\mu_B$	23	21
Fe Fe	$\rightarrow \rightarrow \rightarrow \rightarrow \rightarrow$ $\leftarrow \leftarrow \leftarrow \leftarrow$ Fe ⁼	$\leftarrow \leftarrow \leftarrow \leftarrow \leftarrow$ Fe ⁺⁺	$4\mu_B$	26	22
Fe Co	$\rightarrow \rightarrow \rightarrow \rightarrow \rightarrow$ $\leftarrow \leftarrow \leftarrow \leftarrow \leftarrow$ Co ⁼ Fe ⁼	$\leftarrow \leftarrow \leftarrow \leftarrow \leftarrow$ Fe ⁺⁺ Co ⁺⁺⁺	$5\mu_B$	30	24
Fe Ni	$\rightarrow \rightarrow \rightarrow \rightarrow \rightarrow$ $\leftarrow \leftarrow \leftarrow \leftarrow \leftarrow$ Ni ⁻ Fe ⁼	$\leftarrow \leftarrow \leftarrow \leftarrow \leftarrow$ \rightarrow Fe ⁺ Ni ⁺⁺⁺	$4\mu_B$	30	27

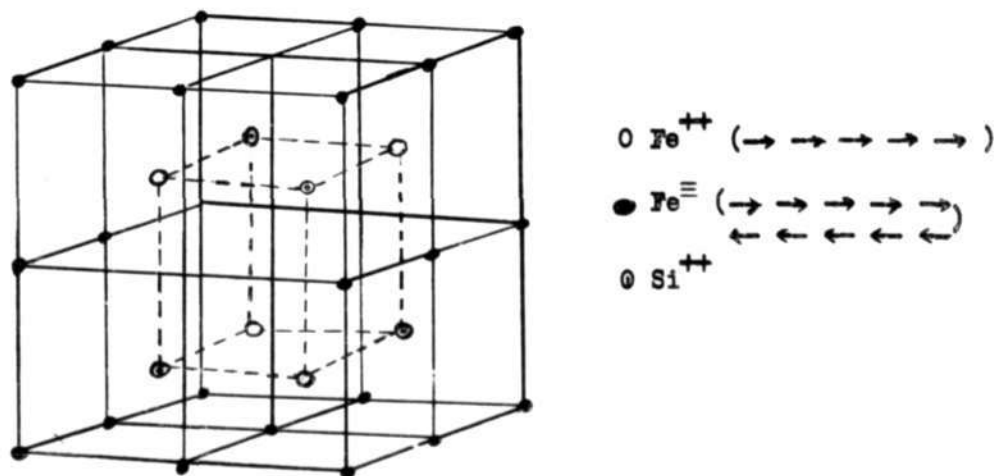
From Table II it can be seen that the net spin per atom pair increases by one Bohr magneton on going from one alloying transition element to the next, until the value $\mu = 5\mu_B$ is reached. Beyond this, the net spin per atom pair decreases by one Bohr magneton. This agrees with equation XL-2.

With the exception of the Fe-Fe (pure iron) system, which was discussed previously, the ionic charge will depend upon whether the alloying element is in the site of atom 1 or atom 2. This is indicated in Table II, with the charge of the iron and alloying ions given for each site. Since the work done to charge the atoms will be greater for higher ionic charge, it is energetically more favorable for the ions to so arrange themselves in the lattice sites as to have the lower ionic charge. The favored position has been listed first in every

case in Table II. In view of this tendency to favor particular sites, one might expect an ordered alloy.

It is possible to have triply charged ions in an iron-cobalt system, since the work required to charge these ions is overcome by the six exchange pairs gained thereby. An iron-nickel system, however, yields a gain of only three exchange pairs, and this is not enough to overcome the ionization energy. Therefore, an iron-nickel system of the form $\text{Fe}^{\equiv} \text{Ni}^{+++}$ cannot exist.

Let us further consider ordered alloys of iron where the alloying element is not a transition element. It was previously shown that the polarity of a given iron atom would be expected to fluctuate rapidly. This will no longer be true if the alloying atom has a strong preference for a particular polarity. This is true for Fe_3Si , where the silicon atoms prefer to occupy the site of an Fe^{++} rather than an Fe^{\equiv} ion. The lattice structure will be as shown in figure 72. Silicon gives up two valence electrons to completely fill the incomplete d shells of the surrounding Fe^{\equiv} ions, changing them to Fe^{\equiv} ions and becoming Si^{++} .

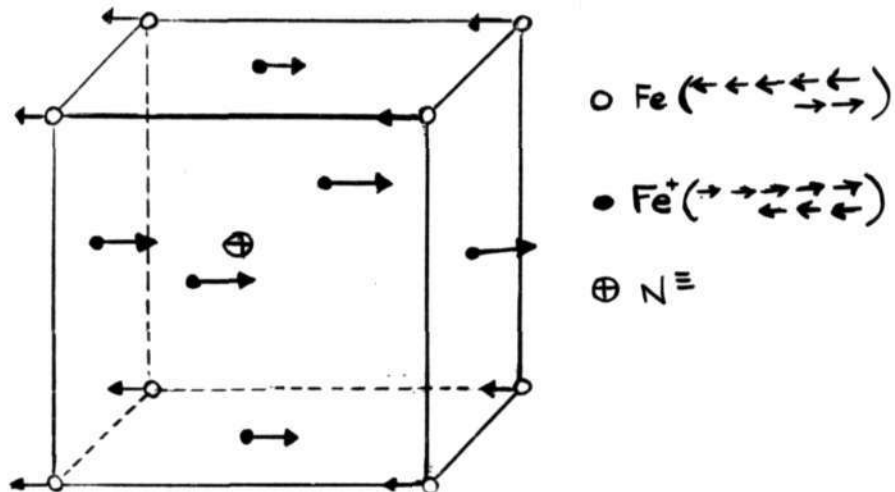


POSTULATED SPIN STRUCTURE OF Fe_3Si

FIGURE 72

As shown in figure 72, the negative iron ions occupy the corner sites of a simple lattice. The positive iron ions occupy half the center sites, and the silicon ions occupy the other half. The Fe^{++} ions have a magnetic moment of $5\mu_B$, while the Fe^{\equiv} and Si have zero magnetic moment. This leads to an average magnetic moment of $5/4 \mu_B$ per atom, which is in agreement with the experimental value.

The iron-nitrogen alloy Fe_4N has a face-centered structure as shown in figure 73. The nitrogen atom is located at the center of each unit cube.



Postulated Spin Structure of Fe_4N

FIGURE 73

The nitrogen atom tends to absorb three electrons, which will be taken from the neighboring Fe atoms. This leads to the face centered structure shown above, with the Fe^+ ions at the faces and the Fe atoms at the corners of the unit cube. Removing a 3d electron from the Fe atom results in a contraction of the 3d shell, thereby reducing the antiferromagnetic interaction between the Fe^+ ions. If this reduction is assumed sufficiently large to permit ferromagnetic coupling of the Fe^+ ions, while the Fe - Fe^+ interaction is ferrimagnetic, we have the spin structure shown in Figure 73. Since there are three Fe^+ ions for each Fe atom, there is a net magnetic moment of $9\mu_B$ per unit cube. This yields an average magnetic moment of $9/4 \mu_B$ per iron atom, which agrees with the experimental value $2.22 \mu_B$.

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