

Memorandum M-1933

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SUBJECT: GROUP 63 SEMINAR ON MAGNETISM, XLIII

To: Group 63 Engineers

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In a recent article,* R. Heikes discusses the Heusler alloys $\text{Cu}_2 \text{Al Mn}$ and $\text{Cu}_2 \text{In Mn}$ from the point of view of both the Heisenberg model and the Zener model. The Heusler alloy lattice structure is shown in figure 80. The distance between the manganese ions is approximately 40% greater in the alloys than in the pure metal.

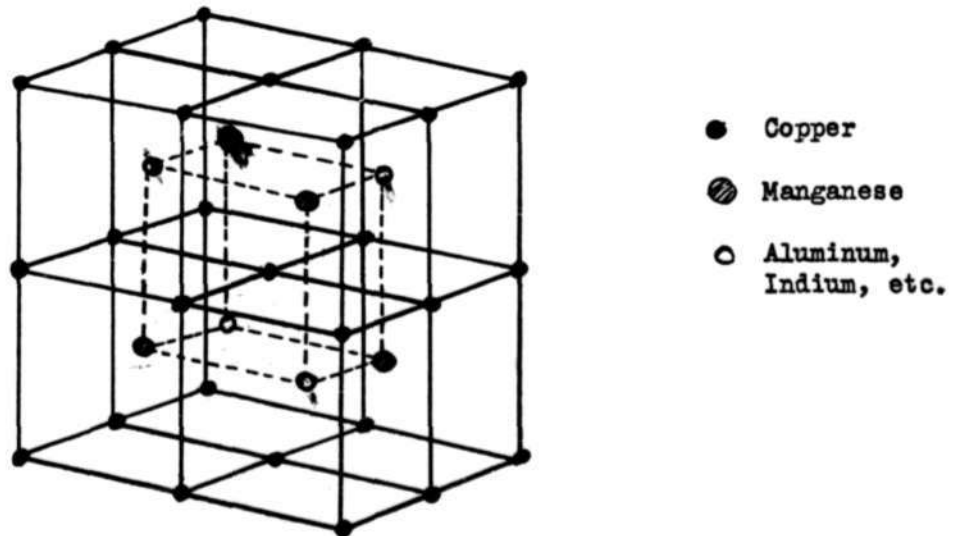


FIGURE 80

* R. Heikes, Phys. Rev. 81, 376 (1951)

The values of the magnetic moment per manganese atom, the Curie temperature, and the distance between manganese ions is given in table I.

TABLE I

MATERIAL	Cu ₂ In Mn	Cu ₂ Al Mn
$\mu_B/\text{Mn atom}$	4.04	4.04
Curie Temp. T _c (°K)	506	603
d _{Mn - Mn} (Å)	4.38	4.17

In both cases the magnetic moment per manganese atom is the same, but the Curie temperatures are different. This difference presumably arises from the fact that the manganese ions are further apart in Cu₂ In Mn. This means there is less interatomic coupling in this case, leading to a reduced Curie temperature.

Heikes makes some rough approximations to calculate the ratio

$$\frac{T_c (\text{Cu}_2 \text{ Al Mn})}{T_c (\text{Cu}_2 \text{ In Mn})}$$

using the Heisenberg and Zener models, and compares the result with the experimental value (1.2).

For the Heisenberg model, Heikes takes the Curie temperature as proportional to the amount of overlap of the atomic wave function. Then

$$T_c \propto |\psi|^4$$

The Hartree wave function $\psi \propto e^{-3.5 \frac{r}{r_0}}$ is taken

where $2r_0$ = distance between Mn ions when they are in equilibrium position

r = distance to center of Mn ion .

Therefore

$$T_c \propto e^{-14 \frac{r}{r_0}}$$

He then obtains

$$\frac{T_c(\text{Cu}_2 \text{ In Mn})}{T_c(\text{Cu}_2 \text{ Al Mn})} = \frac{e^{-\frac{14r_{\text{In}}}{r_0}}}{e^{-\frac{14r_{\text{Al}}}{r_0}}} = e^{\frac{14}{r_0}(r_{\text{Al}} - r_{\text{In}})} = e^{\frac{1.47}{r_0}} = 2$$

According to the Zener model, as has been explained previously (meeting 36), the coupling energy is

$$E = \frac{1}{2} \alpha S_d^2 - \beta S_c S_d + \frac{1}{2} \gamma S_c^2$$

On minimizing E by varying S_c , it was found

$$E = \frac{1}{2} \left\{ \alpha - \frac{\beta^2}{\gamma} \right\} S_d^2$$

Since the $\frac{\beta^2}{\gamma}$ term is the one tending to align the neighboring manganese ions in a ferromagnetic manner, Heikes takes

$$T_c \propto \frac{\beta^2}{\gamma}$$

At meeting 37 we found the values of β and γ per atom. Since Heikes deals with these constants in terms of their value per unit volume, it is necessary to multiply the figures we previously obtained for these coefficients by the number of atoms per unit volume. Then

$$\beta \propto \frac{1}{V}$$

$$\gamma \propto [A\rho^{5/3} - \beta\rho^{4/3}]$$

Using this relationship, Heikes obtains

$$\frac{T_c (\text{Cu}_2 \text{ In Mn})}{T_c (\text{Cu}_2 \text{ Al Mn})} = 1.2$$

In view of the crudeness of this calculation, this close agreement is largely fortuitous. However, it does indicate that the Zener model is preferable.

For the past ten meetings the Zener model of ferromagnetism has been discussed. At this point we briefly summarize the major features of the other models, namely the Heisenberg theory of ferromagnetism based on the Heitler-London model, and the collective electron theory based on the Hartree self-consistent field method.

Heitler-London Model
(atomic orbitals)

This model considers a diatomic molecule, such as a hydrogen molecule (H_2). The wave functions of the individual atoms are known when they are far apart, and their interaction on being brought closer together is treated as a perturbation.⁺

This approximation is good when the individual atoms are far apart. However, when they are close together the perturbation will be much greater than required by this model. Thus the approximation is not too good when the atoms are close to each other.

Heisenberg used this method to arrive at his theory of ferromagnetism. He started with separate lattice elements and considered the interaction of these elements as perturbations.

Hartree - (Fock) Method
(self-consistent field)

When using this method the electron under consideration is assumed to be moving in an average field due to the combined effect of neighboring electrons and nuclei.

This average field value is then used to solve the Schrodinger equation.

This theory leads to the collective electron theory of ferromagnetism. Each electron is part of a statistical system, and is considered as moving in the average field of the rest of the entire system.

⁺ See meeting XXVI

E. P. Wohlfarth^{*}, in an article on collective electron ferromagnetism, objects to certain aspects of the Heisenberg model. These objections are:

1. According to the Heisenberg model of ferromagnetism the exchange integral, which is otherwise negative, must be positive in ferromagnetic materials. Wohlfarth has calculated the exchange integral⁺, and has found it to be negative.
2. The Bloch "spin wave" treatment, which is frequently regarded as the most rigorous and useful extension of Heisenberg's treatment, has been criticized as being based on premises which are probably too idealized to be applicable to actual ferromagnetics. This conclusion is borne out by experimental results.
3. The Heitler-London method is an unjustifiable approximation in metals generally. The collective electron provides the best approximation in this case.

In a paper given at a conference in Wisconsin,^{**} Slater discusses his method of calculation of energy levels. Two general methods have been used for energy level studies; the Heitler-London method and the method of energy bands. The Heitler-London method is better for the simplest molecule, but is not well adapted for complicated molecules or solids.

The method of energy bands follows directly from the self-consistent field method of Hartree (called the collective electron theory by Wohlfarth). The steps needed to give a complete discussion of the atomic structure are:

1. Set up a field in which an electron moves.
2. Solve the Schrodinger equation for electron motion in this field.
3. Compute the charge density arising from the electron motion.
4. Find the average potential and demand that it be consistent with the originally assumed potential.
5. Carry out a perturbation problem, to take account of the structure of the atomic multiplets.

* Wohlfarth, E. P., Philosophical Magazine, Series 7, 40, 703. (1949)

+ Wohlfarth, E. P., Nature, London, 163, 57. (1949)

** Slater, J. C., "Improved Energy Band Calculations for Soft X-Ray Emission," Conference on Applications of X-Ray Spectroscopy to Solid State Problems, University of Wisconsin, Madison. October, 1950.

On applying this method to solids a number of complications arise. First, the potential field in which the electrons are to move in the self-consistent field method must be found. Either the Hartree or Hartree-Fock method may be used.

Solving the Schroedinger equation in the self-consistent field is the next problem. This is difficult in a crystal because of the lack of spherical symmetry. Slater had previously suggested a method for obtaining an approximate solution of this problem. It consisted of writing the solution near each atom as a linear combination of solutions of the spherically symmetric problem, using the coefficients of this combination to satisfy the boundary condition that the function be continuous from atom to atom. This method is adequate for the filled energy level bands, but is inadequate for the higher, unfilled bands.

Most problems discussed using the energy band method have been carried as far as one-electron energy levels and no further. However, one should go further and carry out perturbation calculations to account for multiplet structure. Slater is looking into the general ways of handling this problem.

Slater makes use of the self-consistent field theory to explain the fact that MnO is an insulator despite the fact that it does not have enough electrons to fill the d shell and thus should be a conductor. The Mn^{++} ion has a spin corresponding to all five of its d electron parallel, but the resultant spin of the Mn^{++} ions on adjacent planes are aligned anti-parallel to each other. A self-consistent field calculation shows that if we deal with an electron of a particular spin direction (e.g. \uparrow), the potential energy will be lower in the atoms which have this net spin in the same direction (\uparrow) than it is in the atoms with net spin in the opposite direction. This is indicated in figure 81.

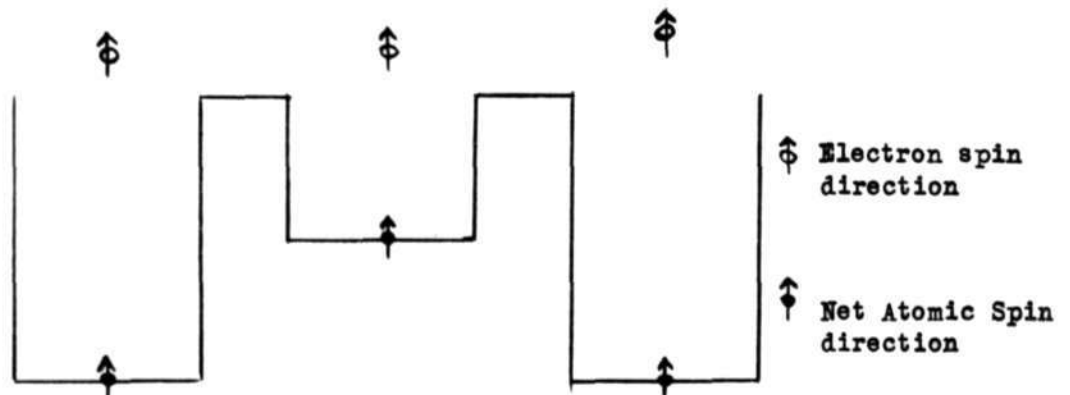


FIGURE 81

From figure 81 it can be seen that the periodicity of the self-consistent potential is double the crystal periodicity, and this brings about a splitting of the energy bands. There will be a lower band, which is filled; an upper band, which is empty; and an energy gap in between. This is just the model of an insulator or semi-conductor as shown in figs. 25a and 25b.

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