SHORT COMMUNICATIONS

FERROMAGNETIC EXCHANGE BETWEEN COUPLED PAIRS OF ELECTRONS*

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Incomplete shells of $3d$ electrons in the first transition series of elements are responsible for the ferromagnetism of these elements, but the parallel coupling of the spins of these electrons remains an assumption in the theory of ferromagnetism. It is required that exchange interaction between the $3d$ electrons of neighbouring atoms should be positive (the sign causing parallel alignment of spins). Mathematically, treatment of ferromagnetic exchange is similar to that of the homopolar chemical bond, in which it is clear that exchange interaction is negative, giving a lower energy for antiparallel spins than for parallel spins. Mathematical difficulties have prevented any adequate demonstration that the reverse is the case in ferromagnetism.

Zener and Heikes (1953) maintained that exchange interactions are always negative, and developed a theory in which parallel alignment of $3d$ electrons occurs by exchange with the conduction electrons. There are some serious objections to this theory and it is more generally assumed that direct coupling between $3d$ electrons is responsible for their parallel spin alignment (Van Vleck 1953). The object of the present note is to point out that the fundamental objection to positive exchange by direct interaction is removed if the elementary magnets are parallel coupled spins which interact in pairs. This requires that each magnetically active atom has two positive holes in its $3d$ shell, with spins coupled parallel by Hund's rule, a suggestion first made by Mott and Jones (1936) for essentially experimental reasons.

The wave function of two electrons, numbered 1 and 2, associated with nuclei a and b is written:

antiparallel spins : $\quad \psi_n = (\psi_a(1)\psi_b(2) + \psi_a(2)\psi_b(1))(\alpha(1)\beta(2) - \alpha(2)\beta(1))$

parallel spins : $\quad \psi_p = (\psi_a(1)\psi_b(2) - \psi_a(2)\psi_b(1))\begin{cases} \alpha(1)\beta(2) + \alpha(2)\beta(1) \\ \text{or } \alpha(1)\alpha(2) \\ \text{or } \beta(1)\beta(2) \end{cases}$

In each wave function the first bracket represents the orbital part and the second bracket the spin part, in which α and β define opposite spin directions. The functions are constructed to be antisymmetric with respect to exchange of the two electrons, as required for the treatment of electrons as Fermi particles.

In the hydrogen molecule problem, ψ_n^2 and ψ_p^2 are multiplied by the Coulomb interaction potential for two nuclei and two electrons and integrated over the volume occupied by ψ_n and ψ_p. (The detailed explanation of this is given by Heitler (1944)). The resulting energy is lower for ψ_n than ψ_p, indicating the negative exchange which causes homopolar bonding.

If the geometry of the wave functions remains essentially unaltered, but *1* and *2* represent parallel coupled pairs instead of individual electrons, and if the coupling within pairs is much stronger than between pairs, we may consider the exchange of pairs and not individual electrons. In this case the pairs behave as bosons rather than fermions, since the wave function of four electrons is symmetric with respect to exchange of pairs, and we must interchange the spin parts of wave functions ψ_n and ψ_p. ψ_n will still give the lower energy but it now gives parallel alignment of all four spins.

The spin wave functions will necessarily be more complicated than has been indicated because the moment of pair *2* in the direction of *1* may be zero as well as ± 2 Bohr magnetons. However, this modification does not need to be given detailed consideration since Van Vleck (1945) established that exchange energy is proportional to the scalar product of spin vectors.

An obvious implication of the present argument is that the existence of spins coupled in even numbers is a necessary prerequisite for ferromagnetism. Mott and Jones (1936) pointed out that there was no objection to this for materials with much less than 2 Bohr magnetons (μ_B) per atom. Materials with $2 \cdot 5$–$3 \cdot 5$ μ_B would contradict the coupled-spin rule, but in the manganese and chromium alloys and compounds listed by Bozorth (1951) the only μ_B numbers much greater than two are nearly four. This gives an immediate explanation for the absence of ferromagnetism in pure manganese, in which the uncompensated spins are probably coupled mainly in threes instead of twos and fours, without postulating a special dependence of exchange energy on atomic spacing. It also allows for the depression of the μ_B number in iron to nearly two, on the Heitler-London-Heisenberg model, without appealing to the band theory of metals to explain the reversed spins.

Metallic chromium provides a contradiction since this could be ferromagnetic with approximately four spins per atom, and gadolinium, with almost exactly seven spins per atom, would still require an indirect exchange mechanism.

References

BOZORTH, R. M. (1951).—" Ferromagnetism." p. 334. (D. Van Nostrand : New York.)

HEITLER, W. (1944).—" Elementary Wave Mechanics." (Oxford Univ. Press.)

MOTT, N. F., and JONES, H. (1936).—" Theory of the Properties of Metals and Alloys." p. 224. (Oxford Univ. Press.)

VAN VLECK, J. H. (1945).—*Rev. Mod. Phys.* **17** : 27.

VAN VLECK, J. H. (1953).—*Rev. Mod. Phys.* **25** : 220.

ZENER, C., and HEIKES, R. R. (1953).—*Rev. Mod. Phys.* **25** : 191.