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AUTHOR

B. H. Brandow

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Theory of the Mott Insulators NiO and CoO*

B. H. Brandow

Theoretical Division
Los Alamos Scientific Laboratory
Los Alamos, New Mexico 87545, U.S.A.

The present subject matter is currently being published¹ in more detail than possible here, and a thorough report will appear elsewhere.² What follows is merely an outline.

We offer a theoretical picture which resolves the main conceptual difficulties of Mott insulators in a very simple and intuitive manner, and which has also yielded some semi-quantitative results in agreement with experiment. We identify Mott insulators with ordinary magnetic insulators, i.e., materials (nominally periodic and stoichiometric) in which local moments and an insulating gap persist above the temperature (T_N or T_C) for the destruction of long-range spin order. (Although the vast majority of such materials are antiferromagnetic, a few ferromagnetic examples are known.) We find that the main features of Mott insulators can be understood within the general framework of the Hartree-Fock (HF) approximation, by considering a suitable variety of different HF solutions. As specific examples we consider NiO, because of its relative simplicity as well as the fact that this has historically been the best-known and most extensively studied example of a Mott insulator, and also CoO, because this focusses attention on an additional problem--that of crystal-field degeneracy. Previous to the present work, there has been no satisfactory explanation for the large insulating (optical) gaps in either of these materials.

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To explain the gaps at zero temperature, we use essentially the antiferromagnetic band theory of Slater.³ The local $\rho^{1/3}$ exchange approximation is unable to account for the large magnitude of the gap in NiO, but a more detailed treatment of the 3d intra-atomic interactions, based on the U, U', J parameters of Kanamori,⁴ is found to be adequate.⁵ We also use the tight-binding hopping integrals obtained by Mattheiss from his band calculations,⁶ thus the 3d electrons are described by an orbitally degenerate version of the familiar Hubbard Hamiltonian. The crystal-field degeneracy problem for CoO is resolved by formally reducing the wavefunction for CoO to a single-determinant form, by means of suitable canonical transformations among the minority t_{2g} orbitals of each Co^{2+} cation. Use of the Kanamori parameters within the HF approximation then leads to the result that the centroids of all of the unoccupied 3d subbands lie higher than their occupied counterparts, by amounts of order U . This explains, for the first time,⁵ why CoO is experimentally so similar to NiO.

We must also explain why these insulating gaps persist for the disordered-spin configurations encountered above T_N . We focus on the prototype system consisting of a lattice of hydrogen atoms. For a sufficiently large one-site Coulomb interaction U , it is plausible to assume the existence of 2^N different self-consistent solutions of the HF equations, solutions which represent insulating configurations in one-to-one correspondence with the 2^N different Ising spin configurations for an N -site system. Although this hypothesis is not at all new,⁷ it has not previously attracted much attention. We have presented the first concrete evidence⁵ in support of this hypothesis. However, the most cogent objection to this elementary picture is that the resulting set of basis functions (the 2^N different N -electron determinants) is not fully orthogonal. This has the

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unfortunate consequence that, in attempting to derive an effective (Heisenberg-like) spin Hamiltonian, one encounters a form of the old non-orthogonality catastrophe. We have resolved this problem⁸ by means of a suitable linked-cluster perturbation expansion,⁹ a degenerate (open-shell) analog of the Brueckner-Goldstone formalism.

Our study also includes a semi-quantitative reconciliation of several kinds of NiO data with the effective 3d hopping integrals obtained by Mattheiss.⁶ This involves the estimation of several orbital rearrangement effects associated with physical 3d holes. Furthermore, a detailed crystal-field analysis of the $3d^{n-1}$ final states has led to far better agreement with the high-resolution XPS data than any previous analyses. A survey of the phase stabilities of various types of HF solutions demonstrates that much of the basic phenomenology of Mott insulators (as evidenced by the generalized phase diagrams for V_2O_3 , NiS_2 - $NiSe_2$, and perovskites) can be qualitatively understood within the present HF framework, when this is supplemented by other known physical effects such as stronger screening in the metallic state.

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