

## LETTER TO THE EDITOR

# Covalent Exchange vs Superexchange in Two Nickel Oxides

John B. Goodenough

Center for Materials Science & Engineering, ETC 9.102, University of Texas at Austin, Austin, Texas 78712-1063

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It is pointed out that the peculiar antiferromagnetic order found in NdNiO<sub>3</sub> and the ferromagnetic coupling of the Ni<sup>2+</sup> in the Li layers of Li<sub>1-x</sub>Ni<sub>1+x</sub>O<sub>2</sub>,  $x \leq 0.08$ , to the ferromagnetic NiO<sub>2</sub> sheets can be accounted for by a shift of the Ni<sup>3+</sup>-O<sup>2-</sup> = Ni<sup>2+</sup>-O<sup>-</sup> equilibrium to the right, which introduces a magnetic coupling carrying the sign of covalent exchange rather than superexchange. © 1996 Academic Press, Inc.

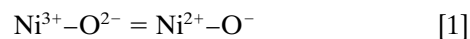
Where transition-metal atoms  $M$  in an oxide insulator have a magnetic moment  $\mu_M = g\mathbf{J}\mu_B$ , the isotropic-symmetric interatomic spin-spin coupling is generally well-described by superexchange perturbation theory; where the perturbation expansion breaks down, it generally describes the sign of the interaction (1). Complex configurations of localized spins are accounted for by considering competitive superexchange interactions and/or antisymmetric Dzialoshinskii terms (2). Therefore it is important to call attention to cases where the theory fails to give the correct sign of the coupling.

The first alternative to superexchange coupling was originally proposed as “semicovalent exchange” (2). Although it may be competitive with superexchange in oxide insulators having a charge-transfer gap (3), semicovalent exchange has been generally ignored because it gives the same sign of the magnetic coupling as the superexchange interaction; the rules for the sign of the superexchange coupling are not violated. On the other hand, magnetic interactions of sign opposite to that predicted from superexchange are well-known in the nitrides and carbides (2, 4); this latter coupling will be referred to as “covalent exchange.” In this letter I call attention to two nickel oxides in which covalent exchange competes with superexchange.

The first example occurs in the perovskite NdNiO<sub>3</sub>; above a first-order transition temperature  $T_t$ , it is metallic with a Stoner enhanced Pauli paramagnetism, whereas below  $T_t$ , it is an antiferromagnetic insulator (5). The magnetic order below  $T_t$  consists of a spin-density wave (SDW)/charge-density wave (CDW) propagating along a

[111] axis with Ni-O-Ni interactions that alternate between ferromagnetic and antiferromagnetic (6). A low-spin octahedral-site Ni(III) ion would have the localized-electron configuration  ${}^2E_g : t_{2g}^6 e^1$ ; stronger Ni-O-Ni interactions would delocalize the single  $e$  electron per nickel atom into a quarter-filled, antibonding  $\sigma^*$  band. In the absence of a cooperative Jahn-Teller deformation (such as occurs in LaMnO<sub>3</sub> with high-spin Mn<sup>3+</sup>-ion configurations  ${}^5E_g : t_{2g}^3 e^1$  (2)), a dynamic Jahn-Teller correlation of empty and half-filled Mn  $e$  orbitals on opposite sides of a bridging oxygen would give a ferromagnetic superexchange interaction (7); in the absence of a SDW/CDW stabilization, a narrow  $\sigma^*$  band that is one-quarter filled would, by extrapolation and experiment (1, 8), be expected to give metallic half-band ferromagnetism. Stabilization of a SDW/CDW below  $T_t$  in NdNiO<sub>3</sub> signals that the antibonding orbitals of  $e$  symmetry have formed a narrow, quarter filled  $\sigma^*$  band in which the magnetic coupling is altered from ferromagnetic by a change in the translational symmetry of the crystal.

In order to account for the altered magnetic order, it is noted that NiO is claimed (9) to be a charge-transfer-gap insulator with, in an ionic model, the Ni<sup>3+</sup>/Ni<sup>2+</sup> redox couple lying below the top of the O  $2p$  band. Although a larger Madelung energy at an octahedral-site Ni(III) may or may not invert this ordering, strong hybridization raises the antibonding  $\sigma^*$  energies to the top of the valence band; the relative amounts of Ni  $e$  and O  $p_\sigma$  character in this band are comparable, so the  $\sigma^*$  band associated with a low-spin Ni(III) ion cannot be properly described with an ionic model. On the other hand, the ability to charge the Ni(OH)<sub>2</sub> cathode of a Cd-Ni battery to NiOOH with little O<sub>2</sub> evolution indicates that the surface reaction



is close to equilibrium; attack by water of a surface O<sup>-</sup> ion to evolve O<sub>2</sub> sets in on crossing from the Ni<sup>3+</sup>/Ni<sup>2+</sup> to the Ni<sup>4+</sup>/Ni<sup>3+</sup> redox couple (10). The possibility of biasing the

equilibrium reaction [1] to either the left or the right at an octahedral site Ni(III) in an oxygen array suggests stabilization of a SDW/CDW in NdNiO<sub>3</sub> in which reaction [1] is shifted alternately to the right and to the left, thereby stabilizing holes on the oxygen of alternate NdO<sub>3</sub> planes. With 2/3 antibonding  $p_{\sigma}$  orbitals per oxygen atom, we may then characterize the CDW/SDW as a Ni<sup>2+</sup>: $t_2^6e^2$  array with Ni<sup>2+</sup> ions separated alternately by covalent and ionic Ni–O–Ni interactions. The “ionic” Ni<sup>2+</sup>–O<sup>2-</sup>–Ni<sup>2+</sup> interactions  $\uparrow - \uparrow \downarrow - \downarrow$  are antiferromagnetic; they carry the sign of the superexchange interactions. The covalent Ni<sup>2+</sup>–O<sup>1.33-</sup>–Ni<sup>2+</sup> interactions carry the sign of the covalent interactions:  $\uparrow - \downarrow - \uparrow$ .

My second example is taken from the paper by Yamaura *et al.* (11) in this issue. Stoichiometric NaNiO<sub>2</sub> consists of close-packed layers of octahedral-site Ni(III) atoms sharing common edges. In these planes, there are only 90° Ni–O–Ni interactions, so the  $e$  orbitals on neighboring Ni atoms are orthogonal to one another. Electron spins in orthogonal orbitals couple ferromagnetically via direct potential exchange, and the NiO<sub>2</sub> sheets are ferromagnetic. The Ni–O–O–Ni interactions between NiO<sub>2</sub> sheets across a Na<sup>+</sup> plane are weakly antiferromagnetic, so NaNiO<sub>2</sub> is a metamagnet (12). Isostructural LiNiO<sub>2</sub>, if perfectly ordered, can be expected to behave similarly; however, perfect order is difficult to achieve. What Yamaura *et al.* appear to have shown with their study of Li<sub>1-x</sub>Ni<sub>1+x</sub>O<sub>2</sub> ( $0 \leq x \leq 0.08$ ) is that, for small values of  $x$ , the Ni atoms in the Li layers not only couple the ferromagnetic NiO<sub>2</sub> sheets ferromagnetically, but they may also couple their own spins parallel to those in the sheets contrary to what is predicted from superexchange theory. The nickel in the Li layer will be Ni<sub>Li</sub><sup>2+</sup>. However, if each of its formal Ni<sub>Li</sub><sup>2+</sup>–O<sup>2-</sup>–Ni(III) bonds undergoes a shift of the equilibrium reaction to the right, then we would have 180°



linkages across the Li<sup>+</sup>-ion plane with all the nickel spins coupled parallel to one another via covalent-exchange coupling rather than superexchange/semicovalent-exchange coupling.

We may anticipate other examples of transitions from superexchange/semicovalent-exchange to covalent-exchange coupling, particularly in the chalcogenides.

#### ACKNOWLEDGMENT

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