Walsh, Da Silva, and Wei Reply: In our Letter [1], we demonstrated that the magnetic interactions in ZnO:Co can be understood from band coupling between Co $3d$ states. Within this understanding, and from explicit electronic structure calculations, we showed that the undoped system is antiferromagnetic, consistent with experiment, while the addition of electrons to the formally unoccupied Co t_{2d} level leads to a ferromagnetic (FM) transition [Fig. 1(a)].

Furthermore, we demonstrated that the behavior predicted from band coupling is not reproduced by standard density functional theory (DFT) approaches because the ZnO conduction band (CB) is too low in energy, so that the Co t_{2d} state is not occupied under moderate electron doping conditions. To achieve partial occupation of the Co t_{2d} state, thus instigating ferromagnetism, the Co t_{2d} level should either be below the ZnO CB or lie within the n-type region [Fig. 1(b)], so the doping-induced Fermi level shift (Moss-Burstein effect) can reach the Co t_{2d} level. Indeed, when we corrected the ZnO band gap error [1], we observed an unambiguous FM transition on electron doping. If the state is artificially placed at higher energy by hybrid (HY) or self-interaction-corrected (SIC) functionals, the same behavior can be found, either with very high doping levels [2] or by coupling with defects that lower the state into the n-type region [3] [Fig. 1(c)].

In their Comment [4], Sanvito and Pemmaraju (SP) question the position of the unoccupied Co t_{2d} level. Experimentally, the assignment of the t_{2d} state close to the ZnO CB has been reported on the basis of optical absorption [5,6], magnetic circular dichroism [7] and photoelectrochemical [8] measurements. While the exact position of the state will depend on the charge state of Co, measurement of both the crystal field splitting ($e_d^4 t_{2d}^3 \rightarrow e_d^3 t_{2d}^4$) and the nominal charge transfer level ($d^7 \rightarrow d^8 + h^{\bullet}_{\mathrm{ZnO}}$) places it below the intrinsic ZnO CB [5,7,8]. Therefore, there is no justification that the Co t_{2d} level in ZnO:Co should lie more than 1 eV (HY [2], SIC [3]) above the CB, even before electron doping.

HY and SIC are valuable approaches that go beyond standard exchange-correlation approximations; however, they underestimate the binding energy of the empty Co d states, which is critical for this system. As demonstrated in our Letter, system dependence between the description of $3d$ transition metal oxides exists. Indeed, time-dependent HY-DFT calculations [9] overestimated the Co $^4A_2 \rightarrow {}^4T_2$ transition in ZnO:Co quantum dots, despite providing a good description of the ZnO band gap itself.

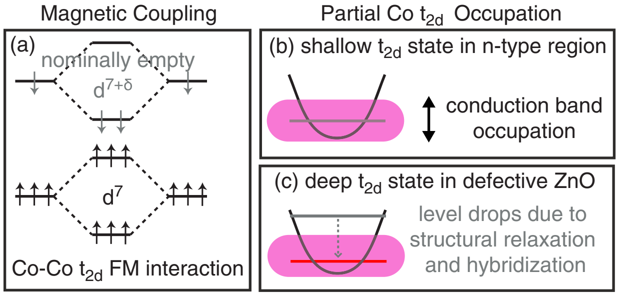

FIG. 1 (color online). Mechanism for FM coupling and scenarios for partial occupation of the Co t_{2d} state.

Finally, SP claim that specific intrinsic defects are needed to instigate ferromagnetic coupling as Co is "insensitive" to electron doping. Although donor defects will be required to provide carriers, direct coupling with point defects is *not* explicitly required [1,2]. Indeed, reports of robust electron-mediated ferromagnetism in ZnO:Co are abundant experimentally within both intrinsic (e.g., Zn$_i$ [10]) and extrinsic (e.g., Ga$_{\mathrm{Zn}}$ [11]) doping approaches. These support a more general mechanism of magnetism in ZnO:Co in stark contrast to one relying on oxygen vacancies alone [3]. Formation of a [Co$_{\mathrm{Zn}} - V_{\mathrm{O}}$] complex is predicted to increase the binding energy of the Co minority spin e_d state by 0.9 eV relative to a tetrahedral Co$_{\mathrm{Zn}}$ substitution [3]; however, no conclusive experimental data so far support the coexistence of two Co coordination environments.

In conclusion, the proposed magnetic coupling model is general and qualitatively independent of how the Co t_{2d} level is occupied. The preceding Comment merely emphasizes one point from our Letter: "Improvement in the treatment of exchange-correlation effects in DFT is required to accurately treat magnetic doping of semiconductors within a fully *ab initio* framework" as typified by the ZnO:Co system.

Aron Walsh, Juarez L. F. Da Silva, and Su-Huai Wei
National Renewable Energy Laboratory
Golden, Colorado 80401, USA

Received 12 January 2009; published 17 April 2009
DOI: 10.1103/PhysRevLett.102.159702
PACS numbers: 71.20.Nr, 71.15.Mb, 75.10.−b, 75.50.Pp

[1] A. Walsh *et al.*, Phys. Rev. Lett. **100**, 256401 (2008).
[2] E.-J. Kan *et al.*, J. Appl. Phys. **102**, 033915 (2007).
[3] C. D. Pemmaraju *et al.*, Phys. Rev. B **78**, 054428 (2008).
[4] S. Sanvito and C. D. Pemmaraju, preceding Comment, Phys. Rev. Lett. **102**, 159701 (2009).
[5] K. R. Kittilstved *et al.*, Nature Mater. **5**, 291 (2006).
[6] P. Koidl, Phys. Rev. B **15**, 2493 (1977).
[7] D. A. Schwartz *et al.*, Adv. Mater. **16**, 2115 (2004).
[8] W. K. Liu *et al.*, J. Phys. Chem. B **109**, 14 486 (2005).
[9] E. Badaeva *et al.*, New J. Phys. **10**, 055013 (2008).
[10] K. R. Kittilstved *et al.*, Phys. Rev. Lett. **97**, 037203 (2006).
[11] Z. Yang *et al.*, J. Appl. Phys. **104**, 113712 (2008).