Comment on “Theoretical Description of Carrier Mediated Magnetism in Cobalt Doped ZnO”

In this Comment, we question the electron-mediated mechanism for magnetic coupling in Co-doped ZnO recently proposed by Walsh, Da Silva, and Wei [1]. Such a mechanism is based on density functional theory (DFT) calculations within a DFT + $U_d + U_s$ approach. Within this approach, Walsh, Da Silva, and Wei introduce *ad hoc* corrections in order to fit the calculated band structure to what they believe is the experimental one. Unfortunately, this fit is based on a direct mapping of electronic excitation energies from optical experiments onto Kohn-Sham (KS) single particle levels which has no formal justification, thus compromising the predictive power of the work. Also, the proposed model predicts high Curie temperature ferromagnetism in structurally perfect n -doped ZnO:Co samples which is disputed by recent experiments [2].

The central point of contention in the paper is the position of the empty minority Co- t_2 single particle states with respect to the conduction band minimum (CBM) of ZnO. Local approximations to the DFT exchange and correlation functional locate them well within the conduction band, although for the wrong reason; i.e., the ZnO band gap is too small. Hybrid functionals (HY) [3] and self-interaction corrected (SIC) schemes [4] which are free of the ZnO band gap error also place them within the conduction band. This is confirmed by recent GGA + U and nonlocal external potentials calculations by Lany *et al.* [5], who find the empty Co- t_2 level located ~ 0.5 eV above the CBM. Importantly, in all of the above calculations, the transition state energy at which the empty Co- t_2 level starts to be occupied under n -doping lies above the CBM. In contrast, Walsh, Da Silva, and Wei fit the position of the t_2 KS states below the CBM once the ZnO elementary band gap is also corrected. They justify this fit by mapping the KS energy difference between the e and t_2 levels onto the energy of the ${}^4A_2 \rightarrow {}^4T_1$ transition [6] obtained from optical absorption experiments. In particular, an adjustable U_d parameter is employed to correct the position of the Co- $3d$ states. The value of this parameter, however, is tuned in order to reproduce experimental intra- d splittings in Co_3O_4 which also correspond to electronic excitation energies. The above mapping unfortunately has no formal justification as we argue below.

KS eigenvalues, particularly those of empty states, in general do not correspond to single particle energies. Furthermore, even in the case of self-interaction corrected theory, the KS orbital energies turn out to be a good first approximation of the *removal* not the *excitation* energies [7]. Static DFT calculations irrespective of the functional employed are incapable of directly accessing optical transitions involving electron-hole pairs. The charge neutral intra- d ${}^4A_2 \rightarrow {}^4T_1$ ($e_d^4 t_d^3 \rightarrow e_d^3 t_d^4$) transition in Co^{2+} observed experimentally at 1.5–2 eV is one such excitation, and its energy cannot be used to quantitatively ascertain the

position of the unoccupied KS t_2 level in a ground state DFT calculation. Similarly, charge transfer type excitations, such as the intra- d optical transition $t_{2g}(\text{Co}^{3+}) \rightarrow t_2(\text{Co}^{2+})$ in Co_3O_4 used by Walsh, Da Silva, and Wei to tune the U_d parameter, are outside the scope of static DFT. Sophisticated many-body approaches such as the GW + Bethe-Salpeter formalism are required to address these problems to the full extent.

Walsh, Da Silva, and Wei also argue that DFT approaches employing HY and SIC are system dependent and fail to reproduce the experimental intra- d splittings in Co_3O_4 . However, as stated above, such intra- d splittings are not valid performance metrics for assessing static DFT functionals. Furthermore, almost all currently available nonempirical DFT functionals are system dependent to some degree; they do perform better for some material systems than for some others. Nevertheless, we did calculate the intra- d band gap in Co_3O_4 using SIC and obtained a value of 1.9 eV, which is compatible with an optical absorption gap of 1.1–1.65 eV reported in experiments [8].

Finally, regardless of the problem of the t_2 state position, Walsh, Da Silva, and Wei argue that electron doping is the only relevant factor for ferromagnetism in ZnO:Co and therefore that samples free of structural defects should be ferromagnetic at sufficiently large n doping. However, such a simple interpretation is disputed by a large number of experimental results [9–13]. Indeed, recent careful experiments [2], where the microscopic characterization of the samples is extremely accurate, demonstrate no ferromagnetism for doping levels up to $5 \times 10^{20} \text{ cm}^{-3}$ and Co concentrations of 10%. In other words, unless structural or point defects are present in addition to Co, the magnetic state is insensitive to electron doping [4].

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- [1] A. Walsh, J. F. Da Silva, and S.-H. Wei, Phys. Rev. Lett. **100**, 256401 (2008).
- [2] T. C. Kaspar *et al.*, New J. Phys. **10**, 055010 (2008).
- [3] C. D. Patterson, Phys. Rev. B **74**, 144432 (2006).
- [4] C. D. Pemmaraju *et al.*, Phys. Rev. B **78**, 054428 (2008).
- [5] S. Lany *et al.*, Phys. Rev. B **77**, 241201(R) (2008).
- [6] K. R. Kittilstved *et al.*, Nature Mater. **5**, 291 (2006).
- [7] J. P. Perdew *et al.*, Phys. Rev. B **23**, 5048 (1981).
- [8] K. J. Kim *et al.*, Solid State Commun. **127**, 25 (2003).
- [9] M. Gacic *et al.*, Phys. Rev. B **75**, 205206 (2007).
- [10] A. Barla *et al.*, Phys. Rev. B **76**, 125201 (2007).
- [11] P. Sati *et al.*, Phys. Rev. Lett. **98**, 137204 (2007).
- [12] H. Ndilimabaka *et al.*, Chem. Phys. Lett. **421**, 184 (2006).
- [13] N. Khare *et al.*, Adv. Mater. **18**, 1449 (2006).