# Excitonic Pathway to Photoinduced Magnetism in Colloidal Nanocrystals with Nonmagnetic Dopants

Pinchetti, V., Lorenzon, M., Camellini, A., Fasoli, M., Zavelani, M., Meinardi, F. and Brovelli, S. (U. Milan – Bicocca); Di, Q. and Zhang, J. (Beijing Inst. of Technology), Crooker, S. (NHMFL-Los Alamos)

## Introduction

Electronic doping of colloidal semiconductor nanostructures holds promise for future device concepts in optoelectronic and spin-based technologies. $Ag^+$ is an emerging electronic dopant in III-V and II-VI nanostructures, introducing intragap electronic states optically coupled to the host conduction band. With its full 4*d* shell $Ag^+$ is nonmagnetic, and the dopant-related luminescence is ascribed to decay of the conduction-band electron following transfer of the photoexcited hole to $Ag^+$. This optical activation process and the associated modification of the electronic configuration of $Ag^+$ remain unclear. Here, we trace a comprehensive picture of the excitonic process in Ag-doped CdSe nanocrystals and demonstrate that, in contrast to expectations, capture of the photohole leads to conversion of $Ag^+$ to paramagnetic $Ag^{2+}$. The process of exciton recombination is thus inextricably tied to photoinduced magnetism. Accordingly, we observe strong optically activated magnetism and diluted magnetic semiconductor behavior, demonstrating that optically switchable magnetic nanomaterials can be obtained by exploiting excitonic processes involving nonmagnetic impurities.

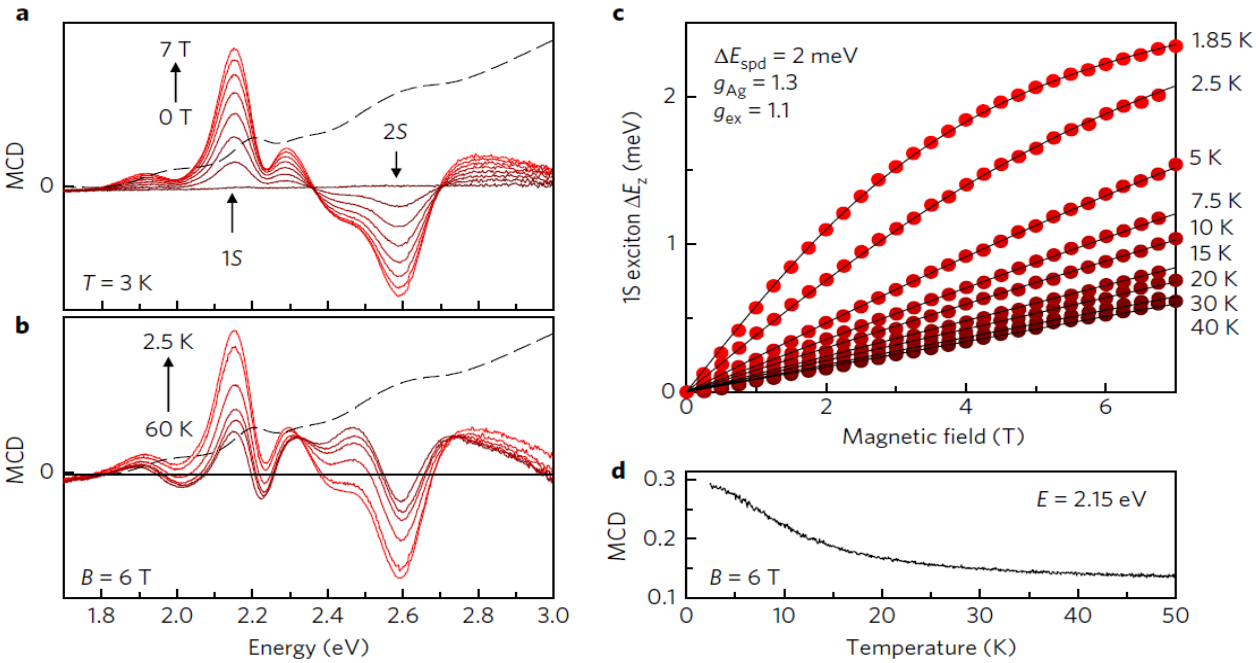


**Figure:** Diluted magnetic semiconductor physics in Ag-doped NCs. **a**, MCD spectra of Ag:CdSe NCs, from which the Zeeman splitting of the 1S exciton is inferred. MCD spectra are shown at 3 K from B=0 to 7 T. **b**, MCD spectra at 6 T, at temperatures from 60 to 2.5 K. The linear absorption spectrum is reported as a dashed black line in **a** and **b**. **c**, Enhanced Zeeman splitting of the 1S band-edge exciton versus magnetic field, at various temperatures. The high field saturation and strong temperature dependence indicate the existence of *sp–d* exchange coupling between the conduction/valence bands of the semiconductor host and a paramagnetic species in the NCs. This species is probably Ag dopants excited by fast localization (capture) of the VB hole. Lines are fits to a Brillouin function using a single set of parameters. **d**, MCD signal of the 1S exciton at 6 T vs. temperature.

## Results and Discussion

We performed magnetic circular dichroism measurements of Ag doped CdSe nanocrystals. In combination with other spectro-electrochemical studies, we have shown that NCs doped with Ag exhibit optically activated paramagnetic properties and concomitant *sp–d* exchange interactions between excitons and Ag dopants, suggesting that optically switchable magnetic nanomaterials can be obtained by exploiting the excitonic processes involving nominally nonmagnetic impurities.

## References

[1] Pinchetti, V. *et al.*, Nature Nanotechnology **13**, 145-151 (2018).