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## High-Frequency EPR and ENDOR Spectroscopy on Semiconductor Quantum Dots

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### Abstract

It is shown that high-frequency electron paramagnetic resonance (EPR) and electron-nuclear double resonance (ENDOR) spectroscopy are excellent tools for the investigation of the electronic properties of semiconductor quantum dots (QDs). The great attractions of these techniques are that, in contrast to optical methods, they allow the identification of the dopants and provide information about the spatial distribution of the electronic wave function. This latter aspect is particularly attractive because it allows for a quantitative measurement of the effect of confinement on the shape and properties of the wave function. In this contribution EPR and ENDOR results are presented on doped ZnO QDs. Shallow donors (SDs), related to interstitial Li and Na and substitutional Al atoms, have been identified in this material by pulsed high-frequency EPR and ENDOR spectroscopy. The shallow character of the wave function of the donors is evidenced by the multitude of ENDOR transitions of the  $^{67}\text{Zn}$  nuclear spins and by the hyperfine interaction of the  $^7\text{Li}$ ,  $^{23}\text{Na}$  and  $^{27}\text{Al}$  nuclear spins that are much smaller than for atomic lithium, sodium and aluminium. The EPR signal of an exchange-coupled pair consisting of a shallow donor and a deep Na-related acceptor has been identified in ZnO nanocrystals with radii smaller than 1.5 nm. From ENDOR experiments it is concluded that the deep Na-related acceptor is located at the interface of the ZnO core and the  $\text{Zn}(\text{OH})_2$  capping layer, while the shallow donor is in the ZnO core. The spatial distribution of the electronic wave function of a shallow donor in ZnO semiconductor QDs has been determined in the regime of quantum confinement by using the nuclear spins as probes. Hyperfine interactions as monitored by ENDOR spectroscopy quantitatively reveal the transition from semiconductor to molecular properties upon reduction of the size of the nanoparticles. In addition, the effect of confinement on the g-factor of SDs in ZnO as well as in CdS QDs is observed. Finally, it is shown that an almost complete dynamic nuclear polarization (DNP) of the  $^{67}\text{Zn}$  nuclear spins in the core of ZnO QDs and of the  $^1\text{H}$  nuclear spins in the  $\text{Zn}(\text{OH})_2$  capping layer can be obtained. This DNP is achieved by saturating the EPR transition of SDs present in the QDs with resonant high-frequency microwaves at low temperatures. This nuclear polarization manifests itself as a hole and an antihole in the EPR absorption line of the SD in the QDs and a shift of the hole (antihole). The enhancement of the nuclear polarization opens the possibility to study semiconductor nanostructures with nuclear magnetic resonance techniques. © 2010 The Author(s).

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