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Shallow Donors in Semiconductor Nanoparticles: Limit of the Effective Mass Approximation

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The spatial distribution of the electronic wave function of a shallow, interstitial Li donor in a ZnO semiconductor nanocrystal has been determined in the regime of quantum confinement by using the nuclear spins as probes. Hyperfine interactions as monitored by electron nuclear double resonance spectroscopy quantitatively reveal the transition from semiconductor to molecular properties upon reduction of the size of the nanoparticles.

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Presently there is great interest in semiconductor nanocrystals because the electronic and optical properties of these structures are strongly affected by quantum confinement owing to the reduced dimensions of these systems. As shown recently, semiconductor nanocrystals can be doped with shallow donors [1,2], which opens up the possibility to study the effect of quantum confinement on their electronic structure. The electronic structure of donors in bulk semiconductors is described successfully within the so-called effective mass approximation, which makes formal the analogy with the hydrogen atom [3,4]. Intuitively one would expect that this effective mass approximation will no longer be valid when the dimensions of the nanoparticle are of the order of or smaller than the Bohr radius $a^* = a_0[\varepsilon_r/(m^*/m_0)]$ of the 1s-type, electronic envelope wave function in the bulk material. Here a_0 is the Bohr radius of the hydrogen atom, ε_r is the dielectric constant of the material, m^* is the effective mass of the electron, and m_0 is the free-electron mass. First, the concept of an effective mass will lose its significance because of the spatial limitations of the periodic crystal structure. Second, the use of a dielectric constant is no longer allowed because the Lorentz relation, which leads to the definition of the dielectric constant for a bulk crystal, does not hold for a nanoparticle.

To analyze the validity of the effective mass approximation in the regime of quantum confinement, we have carried out a study of the shape of the electronic wave function of the shallow interstitial Li donor in ZnO nanocrystals. Recently, we have demonstrated that in ZnO nanocrystals shallow donors can be created by the introduction of interstitial Li and Na atoms [2]. The experimental proof was provided by electron paramagnetic resonance (EPR) and electron nuclear double resonance (ENDOR) experiments at liquid-helium temperatures. Evidence for the shallow character of these donors was provided by the hyperfine interaction of the donor electron with the ^{7}Li and ^{23}Na nuclei and by the multitude of ^{67}Zn ENDOR lines. For the Li-doped nanoparticles, an increase of the hyperfine interaction with the ^{7}Li nucleus and with the ^{1}H nuclei in the Zn(OH)$_2$ capping layer was observed proportional to R^{-3} (R being the radius of the ZnO core) when reducing the radius of the nanoparticles from 2.2 to 1.6 nm. The R^{-3} dependence was explained by assuming that the effective mass approximation is still valid for these particles because their radii are larger than the Bohr radius $a^* =$ 1.5 nm. It was assumed that the 1s-type electronic envelope wave function remains contained in the ZnO core and that only a small fraction of this wave function penetrates into the Zn(OH)$_2$ capping layer.

In this Letter we present the results of an EPR and an ENDOR study of Li-doped ZnO nanocrystals with radii varying between 3.0 and 1.1 nm, i.e., considerably larger and smaller than the Bohr radius $a^* = 1.5$ nm. This study was carried out on freestanding hydroxyl-capped ZnO nanocrystals in the form of dry powders. The preparation of these particles and the measurement of their diameters has been described in our previous Letter [2]. Great attention was given to the measurement of the dimensions of the nanocrystals that were determined with the help of transmission electron microscopy (TEM) and x-ray diffraction (XRD). The TEM measurements yield the total size with a standard deviation of about 0.2 nm. The XRD measurements give the size of the ZnO core with a similar precision. From an analysis of these measurements of, at average, 86 nanocrystals we conclude that the average width of the Zn(OH)$_2$ capping layer is 0.3 nm. This thickness corresponds to one Zn(OH)$_2$ monolayer. In particular, for the nanocrystals with radii smaller than 1.5 nm the growth was very fast and quickly arrested by precipitation. Consequently, inhomogeneities in the capping layer thickness cannot be excluded. The EPR and ENDOR experiments were performed at 1.6 K on a pulsed 95 GHz EPR/ENDOR spectrometer [5].

Figure 1 shows how the splitting of the two ^{7}Li hyperfine components observed in the ENDOR spectrum varies as a function of the radius R of the ZnO core of the nanoparticles. This splitting is equal to the isotropic hyperfine interaction of the unpaired electron spin with the ^{7}Li nuclear spin and is thus proportional to the density of the electronic wave function at the position of the Li$^+$ core. This Li$^+$ core is considered to be at (or near) the center of the ZnO nanoparticle, based on the small size of the hydrogen hyperfine interaction. In the same figure an $AR^{-3} + B$ curve is plotted (solid line). Down to $R = 1.6$ nm the experimental results follow quite closely this dependence while for smaller radii there is a deviation to smaller *values.*

In Fig. 2, in a plot similar to that in Fig. 1, the width of the ENDOR line of the ^{1}H nuclei in the Zn(OH)$_2$ capping layer is shown as a function of R. This width is taken as a measure of the distribution of the hyperfine fields in the capping layer. For particles with R between 2.2 and 1.5 nm, the R^{-3} dependence describes the experimental data, but for smaller radii the width of the ENDOR line seems no longer to increase.

Figures 1 and 2 reveal a considerable spread in the observed hyperfine splitting of the ^{7}Li nuclear spin and the width of the ENDOR line of the ^{1}H nuclear spins for particles with radii smaller than 1.5 nm. We mention three possible causes for this effect. First, the variation in the diameter of these particles, which is about 0.2 nm as observed in the TEM and XRD measurements. This variation also causes a broadening of the EPR line because the g value depends on the size of the particle as a result of the confinement of the wave function [6]. Second, the XRD diffraction patterns indicate that the particles are not perfectly spherical, and this affects the shape of the wave function. Third, there is a relatively large variation in the homogeneity and thickness of the capping layer of the particles with radii smaller than 1.5 nm because of the quick growth and arrestment in the preparation procedure.

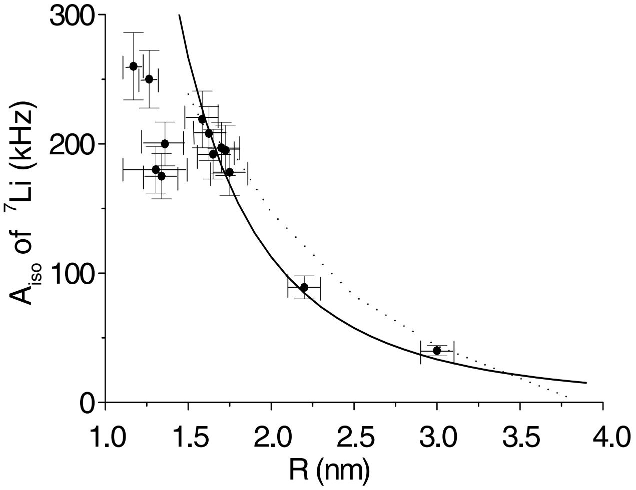

FIG. 1. The isotropic hyperfine interaction $A_{\rm iso}$ of the ^{7}Li nuclear spin of the shallow Li donor in nanoparticles of ZnO with radii between 3.0 and 1.1 nm. The black dots indicate the hyperfine splitting as observed in the ENDOR spectra at $T = 1.2$ K. The error bar in the values of $A_{\rm iso}$ is estimated from the noise in the ENDOR spectra. The variation in the size of the particles is derived from TEM and XRD measurements. The solid line is a least-squares fit to the measured values of $A_{\rm iso}$ for the particles with radii between 3.0 and 1.5 nm using the function $AR^{-3} + B$ with $A = 745.4$ kHz(nm)^3 and $B = 10$ kHz. The dotted line represents the electron density at the position of the Li core as calculated with the model described in the text. (Note that R refers to the radius of the nanoparticle, while the "size" in Ref. [2] refers to the diameter $2R$).

To test whether the observed size dependence of the density of the wave function at the ^{7}Li nucleus in the ZnO core and its distribution in the Zn(OH)$_2$ capping layer can be explained with the effective mass approximation, we have introduced the following trial wave function with appropriate boundary conditions to simulate the envelope function of the shallow donor electron:

$$\Psi(r) = C\exp\{-r/a\}, \qquad (0 < r < R), \tag{1}$$

$$\Psi(r) = D(R_0 - r)/(R_0 - R)\exp\{-r/a\}, \quad (R < r < R_0). \tag{2}$$

Here R indicates the radius of the (spherical) ZnO core and $(R_0 - R)$ the thickness of the Zn(OH)$_2$ capping layer. The preexponential factor in (2) makes the density at the sur-

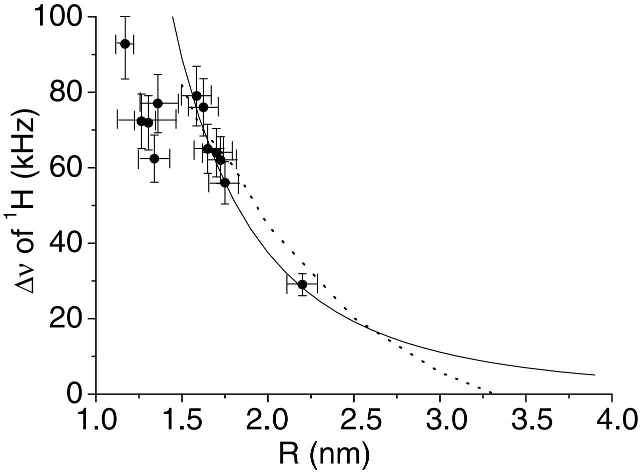

FIG. 2. The width of the ENDOR line of the ^{1}H nuclear spins in the Zn(OH)$_2$ capping layer of ZnO nanoparticles with various radii. The black dots indicate the linewidth as observed in the ENDOR spectra at $T = 1.2$ K. The error bars are obtained in a similar fashion as in Fig. 1. The solid line is a least-squares fit to the measured values of the linewidth for the particles with radii ranging from 2.2 to 1.5 nm using the function $AR^{-3} + B$ with $A = 276.8$ kHz(nm)^3 and $B = 3$ kHz. The dotted line represents the electron density at the ZnO/Zn(OH)$_2$ interface as calculated with the model described in the text.

face of the capping layer zero. The condition of continuity of this function at the $ZnO/Zn(OH)_2$ interface yields $C = D$. The attraction of the functional forms (1) and (2) is that an analytical expression can be found for the total energy E by an elaborate but straightforward partial integration procedure of the two Schrödinger equations corresponding to

$$H_1 = \{-(\hbar^2/2m_1^*)\nabla^2 - (e^2/4\pi\varepsilon_0\varepsilon_1 r)\}, \quad (0 < r < R), \tag{3}$$

$$H_2 = \{-(\hbar^2/2m_2^*)\nabla^2 - (e^2/4\pi\varepsilon_0\varepsilon_2 r)\} + V, \quad (R < r < R_0). \tag{4}$$

Here m_1^* and m_2^* are the effective masses of the electron in ZnO and $Zn(OH)_2$, respectively, and ε_1 and ε_2 the dielectric constants of the two materials. V is the potential difference between the two materials. The normalization of the total wave function (1) and (2) leads to a (complicated) analytical expression for C. The value of "a" of the confined electronic envelope wave function is found by a variational procedure in which the total energy E is calculated numerically and minimized with respect to a. In this calculation the following (bulk) parameters are used: $m_1^* = 0.3m_0$ [7], $m_2^* = 0.7m_0$, $\varepsilon_1 = 8.65$ [7], $\varepsilon_2 = 6.5$, and $V = 1$ eV. The values for a and C so obtained allow us to calculate the density of the wave function at the center of the ZnO core, where the Li nucleus is supposed to be located, and at the interface of the ZnO core and the $Zn(OH)_2$ capping layer.

In Fig. 1 the variation of the density of the electronic wave function at the position of the ^{7}Li nucleus, as calculated with the method described above, is indicated by the dotted line. Between $R = 3$ and $R = 1.5$ nm the calculated variation of the density at the Li^+ core deviates somewhat from the observed dependence of the hyperfine interaction with the ^{7}Li nucleus. For values of R smaller than 1.5 nm no stable solution was found; i.e., no minimum could be found in the total energy as a function of a when using the experimentally determined average thickness of the capping layer $(R_0 - R) = 0.3$ nm. Stable solutions were obtained only for unrealistic values of $(R_0 - R) > 2.0$ nm.

In Fig. 2 the variation of the calculated density of the wave function at the interface of the ZnO core and the $Zn(OH)_2$ capping layer for the particles with radii between 2.2 and 1.5 nm is indicated by the dotted line. This calculated value has been assumed to be proportional to the distribution of hyperfine fields experienced by the ^{1}H nuclei in the $Zn(OH)_2$ layer and thus to the linewidth of the ^{1}H ENDOR line. The calculated variation of the density deviates somewhat from the observed dependence of the hyperfine fields of the ^{1}H nuclear spins.

To check how the choice of the four parameters m_1^*, ε_1, m_2^*, and ε_2 affects the results of the numerical calculation, we have varied the values for the effective masses and dielectric constants. The values $m_1^* = 0.3m_0$ and $\varepsilon_1 = 8.65$ used in the calculation are taken from our previous publication [7]. More recent values are found in the review paper by Meyer *et al.* [8]: $m_1^* \parallel c = 0.28m_0$, $m_1^* \perp c = 0.24m_0$, $\varepsilon_1 \parallel c = 8.75$, and $\varepsilon_1 \perp c = 7.8$. When using these values for m_1^* the resulting change in a is less than 4% while for ε_1 the change in a is less than 2%. Unfortunately the effective mass and the dielectric constant of $Zn(OH)_2$ are not known. From a comparison with the known values for SiO_2 and KOH, m_2^* was estimated between $0.7m_0$ and $0.9m_0$ and ε_2 between 6 and 12. When using these minimum and maximum values variations of a were found of less than 2%. The choice of $V = 1$ eV is estimated from the band gap of the hydroxides and is considered to be a minimum value. Larger values of V resulted in insignificant changes of a. These findings indicate that the results of the calculations are not affected seriously by the choice of parameters.

Our simple analytical model based on the effective mass approximation does not give a stable solution for the electronic wave function of shallow donors in the quantum confinement regime, i.e., in semiconductor nanocrystals with radii of the order of or smaller than the Bohr radius in the bulk material. We give two reasons for this failure. First, it is not permitted to use the bulk value for the effective mass of the electron. This parameter reflects the effect of the periodic potential of a (infinite) semiconductor crystal and this approximation breaks down for the nanometer-sized nanocrystal. In other words, the allowed

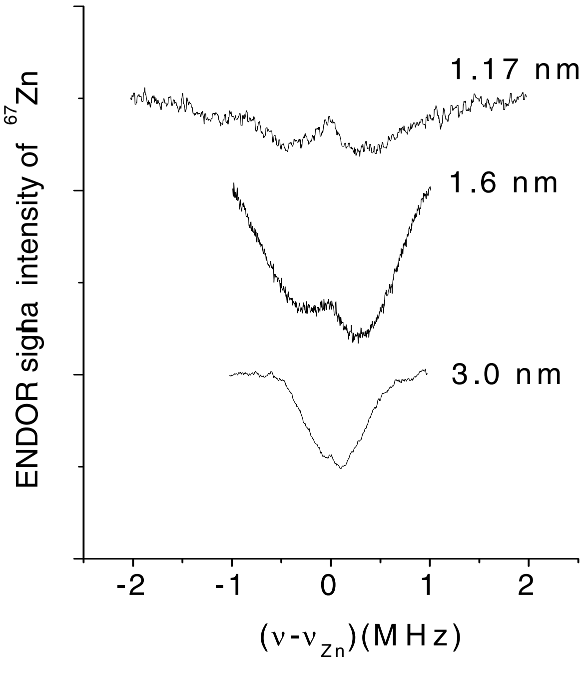

FIG. 3. The ENDOR spectra of the $^{67}Zn(I = 5/2)$ nuclear spins in the ZnO nanoparticles with radii of 1.17, 1.6, and 3.0 nm. Each spectrum consists of many unresolved lines placed symmetrically around the Zeeman frequency of the ^{67}Zn nuclear spins at 9.2 MHz.

values for the wave vector **k** become discrete and the energy eigenvalues are those for an electron of mass m_0 in a box. Second, the definition of a dielectric constant, as a consequence of the Lorentz relation, does not apply to our nanocrystal. As demonstrated by Öğüt *et al.* [9], the effective screening function in a confined system depends on the size of and on the position in the nanoparticle. We believe that an appropriate description of the electronic wave function should be found by using molecular-cluster-type calculations as carried out recently by Melnikov and Chelikowsky [10] for the electronic wave function of shallow P donors in Si nanoparticles.

In addition to the hyperfine interactions with the ^{7}Li and ^{1}H nuclei, information is also supplied by the hyperfine interactions with the ^{67}Zn nuclei. In Fig. 3 the ENDOR spectra of the ^{67}Zn nuclei are presented (symmetrically placed around the ^{67}Zn Zeeman frequency at about 9.2 MHz) for ZnO particles of various diameters. The remarkable observations are that the ENDOR band broadens upon size reduction and develops a dip around the Zeeman frequency of the ^{67}Zn nuclear spins. The dip becomes more prominent and broader when the radius of the ZnO core is reduced from $R = 3.0$ via 1.6 to 1.17 nm. The broadening of the ENDOR band tells us that the maximum density of the electronic wave function increases when reducing the size of the nanoparticles. The disappearance of the ENDOR signals close to the Zn Zeeman frequency, which corresponds to a virtual zero density of the electronic wave function, shows that the density of the envelope wave function at the interface also increases as a result of the confinement. In other words, the dip in the ENDOR spectrum indicates that for the small particles, even at the interface, the Zn nuclei carry nonzero spin density. This conclusion is in line with our observation that the electronic density at the $ZnO/Zn(OH)_2$ interface, as measured from the linewidth of the ^{1}H ENDOR signal, increases with decreasing size of the particles. It is interesting to note that estimates of the electronic density at the $ZnO/Zn(OH)_2$ interface, using either the width of the dip in the ^{67}Zn ENDOR signal or the linewidth of the ^{1}H ENDOR signal and using the amplification factors for Zn and H [7], give about the same value. Our conclusion that the electronic density at the surface increases with decreasing size of the nanoparticle is at variance with the results of the calculations of Melnikov and Chelikowsky [10] for the P-doped Si nanoparticles. From these calculations it appears that, upon reduction of the size of the nanoparticles, the density at the surface becomes very small and that the electron density concentrates in the P-Si nearest-neighhbor bond.

It is interesting to mention that the shallow, interstitial Li and Na donors that can be introduced so easily in ZnO nanocrystals have never been observed in bulk ZnO crystals. We suggest that the confinement may play a role in the stabilization of these donors. When extrapolating the hyperfine interaction at the Li nucleus as a function of the radius of the nanoparticle to $R = \infty$, the hyperfine interaction reduces to about 10 kHz. When comparing this value with the hyperfine interaction of 1.4 MHz observed for the interstitial H donor in bulk ZnO [7] we conclude that the density at the interstitial Li core in bulk ZnO is almost 2 orders of magnitude lower. This suggests that the ionization energy for the interstitial Li donor in bulk ZnO is close to zero.

In summary, our results show that we can monitor the change of the electronic wave function of a shallow donor in a ZnO semiconductor nanoparticle when entering the regime of quantum confinement by using the nuclear spins in the semiconductor nanocrystals as probes. Our model, based on the effective mass approximation, does not yield an appropriate description of the electronic wave function when the radius of the nanoparticle is reduced below the Bohr radius. We suggest that molecular, cluster-type calculations should be carried out to describe the observed behavior.

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