Dynamic nuclear polarization of ^{67}Zn and ^{1}H spins by means of shallow donors in ZnO nanoparticles

Sergei B. Orlinskii* and Jan Schmidt
Huygens Laboratory, Leiden University, P.O. Box 9504, 2300 RA Leiden, The Netherlands

Pavel G. Baranov†
Ioffe Physico-Technical Institute, St. Petersburg 194021, Russia

Celso de Mello Donegá and Andries Meijerink
Debye Institute for Nanomaterials Science, Utrecht University, P.O. Box 80.000, 3508 TA Utrecht, The Netherlands
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Dynamic nuclear polarization (DNP) effects are observed of ^{67}Zn ($I=5/2$) nuclear spins in ZnO nanoparticles and of ^{1}H ($I=1/2$) spins of the $Zn(OH)_2$ capping layer. The almost complete polarization of these nuclear spins is achieved by saturating the electron paramagnetic resonance transition of the shallow interstitial Li donor present in the ZnO nanoparticles. The remarkable aspect is that this DNP is caused by an Overhauser mechanism although the phonons mediating the polarization process do not fit into the nanoparticles. An explanation of this DNP process is presented, and it is shown that this allows for a measurement of the distribution of phonon modes in the nanoparticles. The enhancement of the nuclear polarization also opens the possibility to study semiconductor nanostructures with NMR techniques.

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I. INTRODUCTION

Recently we have shown that high-frequency electron paramagnetic resonance (EPR) and electron nuclear double resonance (ENDOR) are attractive spectroscopic techniques to identify dopants in nanocrystals.[1–3] For instance it proved possible to ascertain that Li forms a shallow interstitial donor in ZnO nanocrystals. Moreover by a study of the hyperfine interaction of the electron spin of this shallow donor with the nuclear spins as a function of the size of the nanocrystal, the effect of confinement on the spatial distribution of the electronic wave function could be measured.

During the EPR experiments on the Li-doped ZnO nanocrystals it was observed that prolonged irradiation of the EPR transition of this donor produces a hole in the EPR resonance line. It was suggested that this hole burning is caused by dynamic nuclear polarization (DNP) of the ^{67}Zn ($I=5/2$) nuclear spins in the ZnO nanocrystal. In a subsequent publication[4] this effect was studied in detail in a bulk ZnO single crystal doped with H which, in analogy to Li, also forms a shallow donor.[5] The surprising conclusion of this study was that the polarization of the ^{67}Zn nuclear spins in this crystal is caused by an Overhauser effect.[6,7] In this process the nuclear polarization arises, upon saturation of the allowed EPR transitions, by a cross relaxation in which the electron spin and nuclear spins undergo flip-flop motions. So far, in semiconductors the Overhauser effect was only observed for conduction electrons or for shallow donors at a relatively high concentration with an exchange interaction that leads to a motional averaging of the EPR resonance line.[8–10] The modulation of the hyperfine interaction between the electron spins and nuclear spins that results from the rapid motion of the electrons creates in these cases the efficient cross relaxation needed for the DNP process. However, in the ZnO single crystal the concentration of donors is so low that the effect of exchange can be ignored. For instance, the EPR line of the shallow H donor is inhomogeneously broadened and the ENDOR transitions of the surrounding ^{67}Zn nuclear spins can be observed without a sign of exchange narrowing. To explain the DNP observed in the ZnO crystal, it was concluded that it is caused by an Overhauser effect that finds its origin in a direct spontaneous-emission-type cross relaxation induced by the zero-point fluctuations of the phonon field. This seems a logical assumption because at the high magnetic field of 10 T and the low temperature of 5 K at which the experiment was carried out the spin-lattice relaxation and the related cross relaxation is dominated by a spontaneous-emission one-phonon process.

At first sight it seems reasonable to assume that the observed dynamic nuclear polarization in the ZnO nanocrystals, induced by the saturation of the EPR transition of the shallow Li donor, is caused by a cross relaxation induced by similar zero-point fluctuations of the phonon field. Here also a spontaneous emission process is expected to dominate the electron-spin relaxation because the experiments were carried out in a magnetic field of 3.4 T and at a temperature of 1.5 K, i.e., the Zeeman splitting of the electron spin is much larger than kT. However the receiving modes of the phonons at 95 GHz, i.e., the frequency at which the EPR experiments are carried out, have an estimated wavelength of about 30 nm, i.e., about ten times larger than the size of the nanoparticles. Thus one would expect that in the case of the nanoparticles the spontaneous-emission type of spin lattice and cross relaxation cannot occur and consequently the DNP should not be an effective process.

To investigate this problem we present here a detailed study of the DNP process in ZnO nanoparticles doped with shallow Li donors using EPR and ENDOR spectroscopy at 95 GHz and low temperature ($T=1.2$ K). It is found that the saturation of the EPR line of the shallow donor not only

leads to a complete polarization of the ^{67}Zn nuclear spins but also of the protons in the $Zn(OH)_2$ capping layer when the radius of the nanoparticles is of the order of magnitude of the Bohr radius of the shallow donor wave function. We suggest a possible explanation for the mechanism of the DNP process in the nanoparticles. An attractive feature is that the enhancement of the nuclear polarization may open the possibility of studying semiconductor nanostructures with NMR techniques that are usually difficult to apply in view of the small thermal polarization of the nuclear spins.

II. EXPERIMENT

Free-standing ZnO nanocrystals with diameters of 2.8, 3.4, 4.0, and 4.2 nm were prepared via a wet chemical method.[1–3] Figure 1(a) shows a TEM image of the ZnO nanoparticles with an average diameter of 3.4 nm (left). The surface of the as-prepared dots is capped by a thin layer (about one monolayer) of $Zn(OH)_2$ and thus the dots consist of a $ZnO/Zn(OH)_2$ core-shell structure [Fig. 1(a), right].

The EPR experiments were performed at temperatures ranging from 1.2–2.0 K using a home-built pulsed EPR spectrometer operating at 95 GHz.[11] The EPR spectra were recorded by detecting the electron-spin-echo (ESE) signal as a function of the magnetic field. ENDOR spectra were obtained by the stimulated-echo pulse sequence.[12] Owing to the high microwave frequency a high spectral resolution in the EPR as well as in the ENDOR spectra is achieved. This high resolution is essential to separate EPR signals of centers with close lying g factors.

III. RESULTS

Figure 1(b) shows the ESE-detected EPR signal of the shallow Li donor in a dry powder of ZnO nanoparticles with a diameter of 4 nm observed at a frequency of 94.9 GHz and a temperature of 1.5 K. Before the EPR experiment ultraviolet (UV) light illuminated the sample at 1.5 K during 30 min to transfer an electron from the deep Na-related surface acceptor in the ZnO nanocrystals to the shallow Li donor to make the two impurities paramagnetic.[3] In the upper curve (1) the EPR line is recorded without microwave preirradiation. The line is slightly asymmetric and its width is caused partly by the anisotropy of the g tensor and partly by the distribution in size of about 10%. The dependence of the g tensor on the size of the nanocrystals is caused by the confinement of the 1s-type electronic wave function of the shallow donor that has a Bohr radius comparable to the radius of the nanoparticles.[13,14] Curve 2 in Fig. 1(b) is recorded immediately after continuous-wave (cw) microwave preirradiation during 3 min with a microwave power of 20 mW at the center of the unperturbed line (1). It is seen that after the irradiation a hole is burnt in the line and that simultaneously a new sharp peak (an "antihole") appears at the low-field side of the hole. The curve (2-1) represents the difference between curves (2) and (1) and clearly shows the antihole that arises in addition to the hole.

The creation of the hole and antihole in the EPR line is caused by dynamic nuclear polarization of the ^{67}Zn ($I=5/2$) nuclear spins and, as we will show below, of the ^{1}H ($I=1/2$) nuclear spins in the $Zn(OH)_2$ capping layer. The polarized nuclear spins create an internal magnetic field and as a result the resonance line of the electron spins, subjected to the microwave irradiation, shifts to a lower external field value resulting in the hole and the antihole in the inhomogeneously broadened EPR line. In the DNP process of shallow H donors in a single crystal of ZnO a similar effect was observed.[4] Since the linewidth of the shallow Li donor in the random sample of ZnO nanocrystals depends to a large extent on the anisotropy of the g tensor, the hole in the line corresponds to electron spins of shallow donors in ZnO particles with a given orientation of their hexagonal crystal axis with respect to the external magnetic field. The hole decays

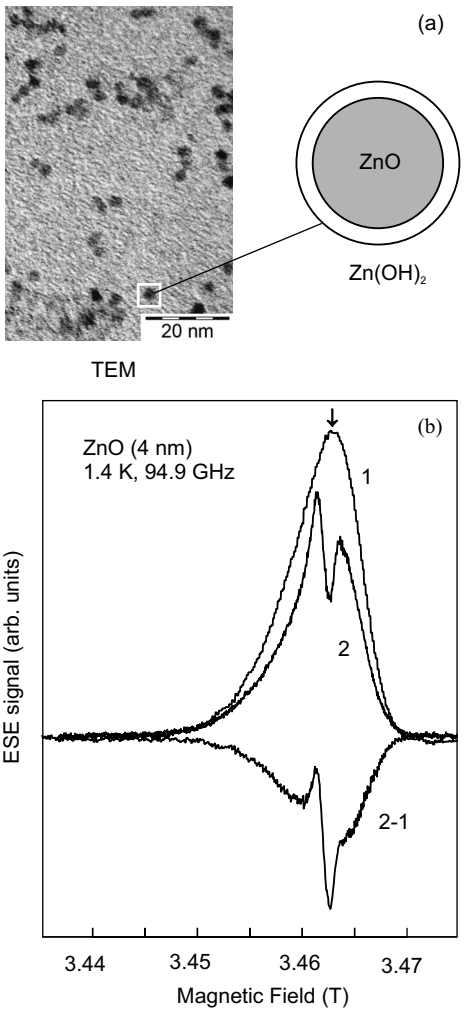

FIG. 1. (a) TEM image of ZnO nanoparticles with a diameter of 3.4 nm (left) and a model of the $ZnO/Zn(OH)_2$ core-shell structure (right). (b) The effect of cw resonant microwave irradiation on the line shape of the ESE-detected EPR spectrum at 94.9 GHz and 1.4 K of the shallow Li donor in a dry powder of ZnO nanocrystals with a diameter of 4 nm. In the upper curve (1) the EPR line is recorded without preirradiation. The spectrum labeled by (2) is recorded immediately after cw microwave irradiation with a power of 20 mW during 3 min at the center of the unperturbed line (1). Curve (2-1) represents the difference between curves (2) and (1). It is seen that a hole is burned and an antihole develops.

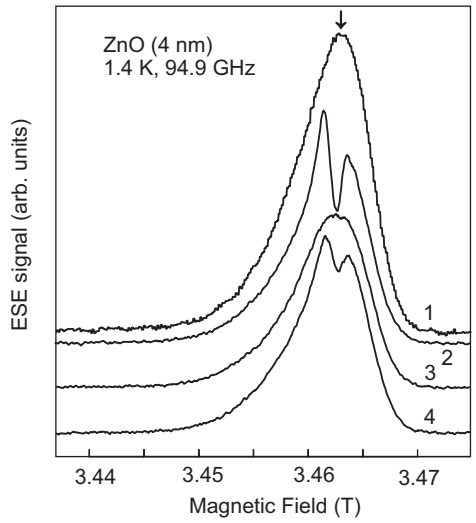

FIG. 2. In this figure the effect is shown of a rotation of the sample of ZnO nanocrystals with a diameter of 3.2 nm on the hole burnt in the EPR line of the shallow Li donor (curve 1). The curve labeled by (2) is recorded immediately after cw microwave irradiation during 3 min with a power 20 mW at the center of the unperturbed line (1). The other curves are recorded after a rotation of the sample over, respectively, 90° (curve 3) and 180° (curve 4). $T=1.4$ K.

slowly and disappears in about 30 min. This disappearance is caused by the nuclear-spin relaxation that gradually restores the nonthermal nuclear-spin polarization to its equilibrium value.

In Fig. 2 the behavior of the hole is shown as a function of the orientation of the sample in the magnetic field. First a hole is burnt in the inhomogeneously broadened EPR line of a sample of ZnO nanoparticles with a diameter of 4 nm with cw microwaves during 3 min at the center of the EPR line (curve 1). The orientation of the sample tube in this experiment is labeled as 0° (curve 2). Subsequently the EPR spectrum is again recorded when the sample tube, containing the ZnO powder, is rotated over 90° (curve 3) and 180° (curve 4), respectively. It is seen that the hole disappears after a rotation of 90° but that after a rotation of 180° the hole reappears at the same position. A decrease in the depth of the hole is caused by the effect of the nuclear spin-lattice relaxation during the time of the measurement of about 20 min. The attractive feature of this experiment is that one can select a particular orientation of nanoparticles in a random sample.

In Fig. 3 it is shown how the hole and the antihole shift through the inhomogeneous EPR line of ZnO nanoparticles with a diameter of 4.2 and 2.8 nm, by exposing the samples to subsequent preirradiations with cw microwaves. In Figs. 3(a) and 3(b) the lowest curve is recorded without preirradiation. The first curve above the lowest one is recorded after cw microwave irradiation at 20 mW during 3 min at the center of the unperturbed line. The next curve is obtained after cw microwave irradiation during 3 min at the peak of the antihole in analogy to similar experiments on the shallow donor in the single-crystal ZnO.[4] This procedure is repeated and finally the antihole stabilizes at a position shifted by 3 mT for the particles with a diameter of 4.2 nm and 7 mT for

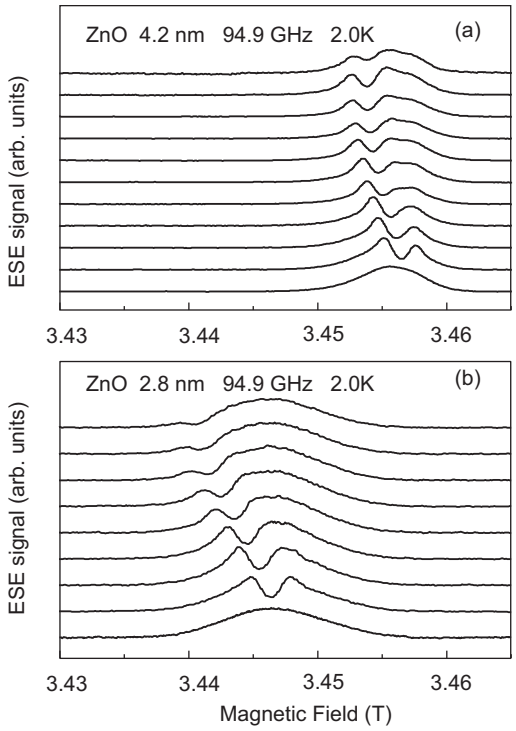

FIG. 3. (a) The shift of the hole in the EPR transition of the shallow Li donor in ZnO nanocrystals with a diameter of 4.2 nm induced by cw microwave irradiation at 94.9 GHz at 2 K. In the lowest curve the EPR line is recorded without preirradiation. The second recording from the bottom is obtained after cw microwave irradiation during 3 min at the center of the unperturbed line. The next curves are observed after cw microwave irradiation during 3 min at the maximum of the antihole of the previous recording. Finally, the antihole stabilizes at a position shifted by 3 mT with respect to the original position. (b) The same experiment as in curve (a) is carried out on the EPR line of the shallow Li donor in ZnO nanocrystals with a diameter of 2.8 nm. Here the antihole stabilizes at a shift of 7 mT with respect to the original line position.

those with a diameter of 2.8 nm. In Fig. 4 the shift of the hole and the antihole versus the number of 3 min cycles of microwave preirradiation is shown for the shallow Li donor in ZnO nanoparticles with diameters of 2.8, 3.4, and 4.2 nm. For comparison a similar curve is shown for the shift of the EPR line of the shallow H donor in a single crystal of ZnO.[4] It is seen that for particles with an average diameter of 4.2 nm the maximum shift is about the same as for the single crystal but that the shift increases considerably when performing the experiments on nanocrystals with diameters of 3.4 and 2.8 nm. In the next section we will present arguments to explain the increase in this shift by DNP of the ^{67}Zn nuclear spins and of the ^{1}H nuclear spins in the $Zn(OH)_2$ capping layer, in combination with the effect of confinement of the electronic wave function of the shallow donor.

The effect on the EPR line of the relaxation of the polarized nuclear spins back to their equilibrium value is visible in Fig. 5. Here the EPR signal is shown of the shallow donor in ZnO nanocrystals with a diameter of 4.2 nm induced by 3 min cw microwave preirradiation (20 mW) at 94.9 GHz at 2 K. In the upper curve, the EPR line is recorded without preirradiation. The second recording from the top is obtained after

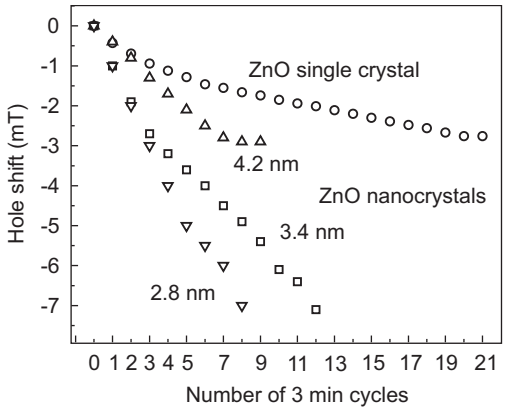

FIG. 4. The shift of the hole and the antihole versus the number of 3 min cycles of cw microwave irradiation in the EPR line of shallow Li donors in ZnO nanocrystals with a diameter of 2.8, 3.4, and 4.2 nm and for shallow H donors in a ZnO single crystal. $T=2$ K.

cw microwave irradiation at the center of the unperturbed line. It is seen that a hole is burned in the center of the line where the irradiation took place. The spectrum labeled by (0) represents the difference between the two upper curves. Similar curves labeled by (4), (9), (13), (27), (40), and (74) are recorded at 4, 9, 13, 27, 40, and 74 min after the preirradiation, respectively. It is seen that slowly the hole and antihole decrease and that the EPR spectrum recovers to its

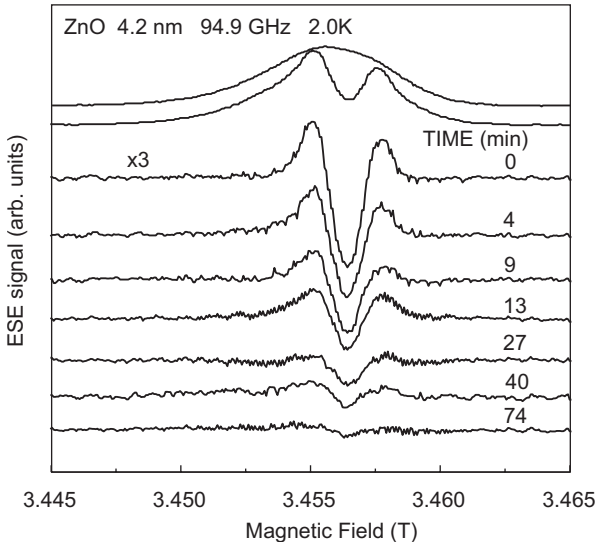

FIG. 5. The relaxation of the nuclear polarization in the EPR signal of the shallow donor in ZnO nanocrystals with a diameter of 4.2 nm as monitored by the evolution of the hole burnt in the EPR line by 3 min cw microwave irradiation (20 mW) at 94.9 GHz at 2 K. In the upper curve, the EPR line is recorded without preirradiation. The second recording from the top is obtained after the cw microwave irradiation. The spectrum labeled by (0) represents the difference between two upper curves. Curves (4), (9), (13), (27), (40), and (74) are recorded a similar way at 4, 9, 13, 27, 40, and 74 min after the preirradiation, respectively. It is seen that slowly the hole and antihole decrease and that the EPR spectrum recovers to its initial unperturbed form.

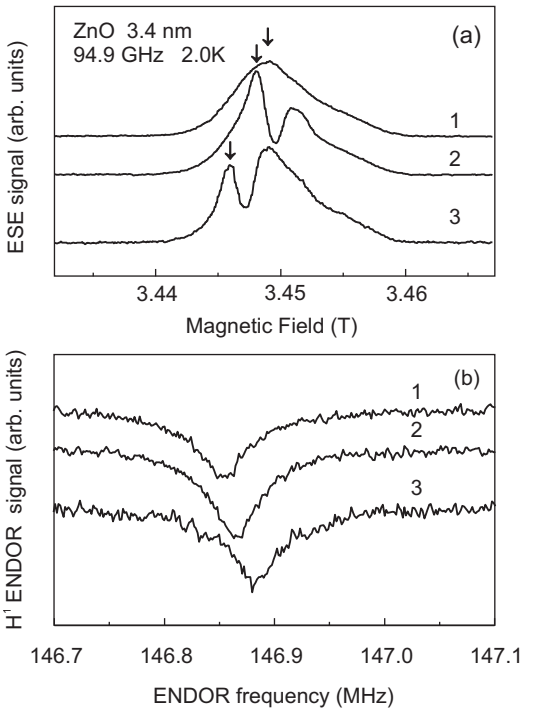

FIG. 6. (a) Curve (1) represents the unperturbed EPR transition of the shallow Li donor in ZnO nanocrystals with a diameter of 3.4 nm. Curve (2) is obtained after cw microwave irradiation during 3 min at the center of the unperturbed EPR line. Curve (3) is recorded after cw microwave irradiation during 3 min at the peak of the antihole in curve (2). The arrows indicate the positions at which the ENDOR spectra displayed in (b) are taken. The temperature is 2 K. (b) The ENDOR spectra of ^{1}H nuclei detected in the EPR transition of the shallow Li donor in ZnO nanocrystals with a diameter of 3.4 nm at different magnetic field positions in the EPR line as indicated in Fig. 6(a).

initial unperturbed form. It takes about 75 min for the hole and antihole to relax to their original zero value. The relaxation of the polarized nuclear spins back to their equilibrium value depends on the nanocrystal size. The relaxation time decreases when decreasing the size of the nanocrystals, e.g., for the ZnO nanocrystal with a diameter of 2.8 nm it takes about 30 min for the hole in the EPR line to relax to its original zero value at 2 K.

To check whether a polarization of the ^{1}H nuclear spins affects the resonance line of the electron spin we have carried out ENDOR experiments on the protons. Curve 1 in Fig. 6(a) represents again the unperturbed EPR line. Curve 2 is the result obtained after 3 min of microwave irradiation at the peak of the line. Curve 3 is recorded after 3 min of microwave irradiation at the peak of curve 2. In Fig. 6(b) the ENDOR signals are presented of the ^{1}H nuclear spins detected in curves 1, 2, and 3 of Fig. 6(a) at the positions indicated by the arrows. First of all it is seen that strong ENDOR signals are obtained around the Zeeman frequency of the ^{1}H nuclear spins indicating that the wave function of the shallow donor extends into the capping layer. Second, the resonance frequency of the ^{1}H nuclear spins shifts to higher frequency when the magnetic field at which the ENDOR experiment is carried out moves to lower field values. We

explain this behavior by the polarization of the ^{1}H nuclear spins, which produce an internal field and thus shift their resonance frequency to higher values.

IV. DISCUSSION

The experiments presented in the previous section demonstrate that the ^{67}Zn as well as the ^{1}H nuclear spins become polarized when saturating the EPR transition of the shallow Li donor in the ZnO nanoparticles. The dynamic polarization of the ^{67}Zn nuclear spins shows the same behavior as observed for the ^{67}Zn spins in a single crystal of ZnO doped with the shallow H donor.[4] In particular the maximum shift of the hole observed in the ZnO nanoparticles with a diameter of 4.2 nm is the same as the shift of the EPR line of the shallow H donor in the single crystal of ZnO. This is reasonable because it was shown that in the case of the ZnO single crystal the maximum shift of 2.8 mT could be simulated by considering the complete polarization of all ^{67}Zn spins in a sphere with a radius of about 2.0 nm.[4] When the diameter of the nanoparticles becomes smaller a considerable increase is observed of the maximum shift of the hole (see Fig. 4).

To understand the increase in the shift of the hole in the ZnO nanoparticles with a diameter of 2.8 nm we have carried out a numerical calculation of the local field produced by a complete polarization of the ^{67}Zn nuclear spins. This calculation was performed in the same way as for the shift of the EPR line observed for the shallow H donor in a single crystal of ZnO.[4] Here we took into account the effect of confinement of the electronic wave function resulting in an increase in the hyperfine interaction with the ^{67}Zn nuclear spins, and the fact that only five shells of Zn atoms have to be considered in the 2.8 nm particles. The resulting shift amounts to 3.0 mT. This shift is almost equal to the value observed for the EPR line of the shallow H donor in a single crystal of ZnO.[4] This is not surprising because the number of polarized ^{67}Zn spins in a nanoparticle with a radius of R is proportional to R^3 whereas the density of the electronic wave function of the shallow donor is proportional to R^{-3}.[2] As a result the decrease in the number of ^{67}Zn nuclear spins, when decreasing the size of the nanoparticle, is compensated in first approximation by the increase in the hyperfine interaction. Thus it looks improbable that the increase in the shift of the hole upon decreasing the size of the nanoparticle is caused by the polarization of the ^{67}Zn nuclear spins.

To investigate whether the increased shift of the hole is related to the ^{1}H spins we have estimated the contribution of polarized ^{1}H nuclear spins in the $Zn(OH)_2$ capping layer. When assuming a monolayer of $Zn(OH)_2$ with completely polarized ^{1}H nuclear spins and a hyperfine interaction of about 100 kHz, as derived from the width of the ENDOR lines in Fig. 6(b), we estimate that these polarized ^{1}H nuclear spins produce a maximum shift of the hole in the EPR line of the 2.8 nm ZnO nanoparticles of about 2 mT. Thus we conclude that the increase in the shift of the hole, when reducing the size of the nanoparticles, is most probably caused by the polarization of the ^{1}H nuclear spins in the $Zn(OH)_2$ capping layer.

The polarization of the ^{67}Zn nuclear spins in the case of the shallow donor in the single crystal of ZnO is caused by an Overhauser effect. Here a cross-relaxation process, in which electron spins and nuclear spins undergo flip-flop motions, transfers the electron-spin polarization to the nuclear spins upon saturation of the electron-spin transition. To make this process efficient a rapid modulation is required of the hyperfine interaction to induce a fast spin-lattice relaxation rate of the electron spins and a fast cross-relaxation rate, i.e., a fast flip-flop motion. In semiconductors this modulation is provided by the rapid motion of conduction electrons or by the exchange interaction of shallow donors that at high concentrations have a sufficient overlap of their wave function. Since the shallow H donors in bulk ZnO have a low concentration and do not show any sign of a rapid exchange it was proposed that the modulation of the hyperfine interaction is caused by the fluctuations of the zero-point vibrations of the phonon system. This seems a reasonable suggestion because at the high magnetic field (10 T) and low temperatures (5 K) at which the experiments were carried out the Boltzmann factor is no less than 20 and the spontaneous emission processes dominate the one-phonon-type spin-lattice relaxation of the electron spins.

In the ZnO nanocrystals only one donor-electron spin is present in a particle and the effect of exchange resulting from an overlap of electronic wave functions can be excluded. Since here the EPR experiments are carried out at 95 GHz in a magnetic field of 3.4 T and at temperatures of 1.5–2.0 K the spin-lattice relaxation is also dominated by spontaneous-emission-type processes. The typical wavelength of phonons at 95 GHz in ZnO nanocrystals required to induce the one-phonon relaxation process of the electron spin of the shallow Li donor is determined by the velocity of sound in this material. When using the value $v=3\times10^3$ ms^{-1} as a reasonable estimate of this velocity one derives that the wavelength of phonons at 95 GHz, the frequency at which the EPR experiments are carried out, is about 30 nm, i.e., about ten times larger than the average size of the nanoparticles. We thus conclude that the phonons required to induce the one-phonon-type spin lattice and cross relaxation do not fit into the particles. The remarkable observation is that the spin-lattice relaxation rates observed for the shallow H donor in the bulk ZnO single crystal and for the shallow Li donor in the ZnO nanocrystal at low temperature are about the same (about 10^3 s^{-1}). To explain the relatively fast one-phonon-type spin-lattice relaxation of the shallow Li donor in the ZnO nanocrystals we propose that in the dry powder, used in the experiments, the particles are in physical contact with each other and that the phonons are not confined to one particle. To check whether this explanation is correct it would be attractive to perform similar experiments on samples of ZnO nanoparticles dissolved in an organic glass. In such a sample the velocity of sound in the ZnO particles is much higher than in the glassy host material and one may expect that phonons will reflect at the interfaces thus leading to a better confinement of the phonons in the ZnO nanoparticles. A measurement of the spin-lattice relaxation of the shallow donor as a function of the size of the nanoparticles could then be used to confirm the validity of this contention and would allow for a measurement of the distribution of phonon modes in the nanocrystals.

V. CONCLUSION

Dynamic nuclear polarization effects have been observed in ZnO nanoparticles. This polarization manifests itself via the creation of a hole and an antihole in the EPR absorption line of the shallow Li donor present in the particles upon irradiation with a resonant microwave field. This effect arises not only from an almost complete polarization of the ^{67}Zn nuclear spins in the ZnO nanoparticle but also of the ^{1}H nuclear spins in the $Zn(OH)_2$ capping layer. The enhancement of the nuclear polarization may open the possibility to study semiconductor nanostructures with NMR techniques.

The nuclear polarization is produced by a spontaneous-emission-type one-phonon cross relaxation that is mediated by the zero-point fluctuations of the phonon system in the ensemble of nanoparticles. It is suggested that a systematic study of this effect as a function of the size of the nanoparticles may allow measuring the distribution of phonon modes in the nanoparticles. For such an experiment to be successful it is necessary to incorporate the nanoparticles in a soft matrix to localize the phonons in the nanoparticles.

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*Present address: Federal Center of Shared Facilities of Kazan State University, 42008 Kazan, Russia.
†pavel.baranov@mail.ioffe.ru

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