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Dynamical nuclear polarization by means of shallow donors in ZnO quantum dots

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ABSTRACT

The almost complete dynamic nuclear polarization (DNP) of nuclear spins has been demonstrated can be achieved in ZnO and AgCl single crystals by saturating the EPR transition of the shallow donor (SD) present in this crystals with using high-frequency (275 and 95 GHz) at low temperatures. DNP effects have also been observed in ZnO quantum dots (QD's) where polarization of ^{67}Zn nuclear spins in ZnO core and of ^{1}H nuclear spins in the $Zn(OH)_2$ capping layer have been obtained by saturating the EPR transition of the SD present in the ZnO QD's. DNP manifests itself via a shift of the EPR lines of SD in bulk ZnO and AgCl crystals and the creation of a hole and an antihole in the EPR absorption line of the SD in QD's. The enhancement of the nuclear polarization opens the possibility to study semiconductor nanostructures with NMR techniques.

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1. Introduction

High-frequency electron paramagnetic resonance (EPR) and electron nuclear double resonance (ENDOR) was shown to be a method of choice for investigation of shallow donors (SD) in wide-band-gap semiconductors (AgCl, ZnO, AlN) [1–4]. This is attractive spectroscopic techniques to identify dopants in single crystals and nanocrystals. Moreover by a study of the hyperfine (HF) 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 nuclear spins in the ZnO nanocrystal. In a subsequent publication this effect was studied in a bulk ZnO single crystal doped with H [5] which, in analogy to Li, also forms a shallow donor.

To investigate this problem we present here a study of the DNP process in ZnO nanoparticles with SD's using high-frequency EPR and ENDOR spectroscopy at low temperature. In addition we will spread our investigations of dynamic nuclear polarization on another system with shallow donors-AgCl crystals. Shallow donors in AgCl single crystals were investigated in detail in Ref. [1], it was identified the split-interstitial structure of the intrinsic shallow donors and the wave-function space distribution was measured up to about 60 shells.

We will suggest a possible explanation for the mechanism of the DNP process in the bulk crystals and nanoparticles. An attractive feature is that the enhancement of the nuclear polarization may open the possibility of studying semiconductor nanostructures with nuclear magnetic resonance (NMR) techniques that are usually difficult to apply in view of the small thermal polarization of the nuclear spins.

2. Experimental

Nominally undoped ZnO and AgCl single crystals were used. Free-standing ZnO nanocrystals with diameters of 2.8, 3.4, 4.0, and 4.2 nm were prepared via a wet chemical method [3]. 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. The SD's were subsequently generated in AgCl and ZnO QD's by radiation from a 100 W mercury arc.

The EPR experiments were performed at temperatures ranging from 1.2 to 10 K using a pulsed EPR spectrometers operating at 275 and 95 GHz. The EPR spectra were recorded by detecting the

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electron-spin-echo (ESE) signal as a function of the magnetic field. ENDOR spectra were obtained by Mims' type the stimulated-echo pulse sequence.

3. Results and discussion

The top panel in Fig. 1(a) shows the ESE-detected EPR spectra of the shallow donors in nominally undoped ZnO single crystal measured at 275 GHz ($T = 4.5$ K). The curve at the right is the unperturbed line which corresponds to $g = 1.956$ [2]. Remarkable effects has been observed after preirradiation with cw microwaves at the center of the line [5]. In Fig. 1(a), top panel, it is seen that

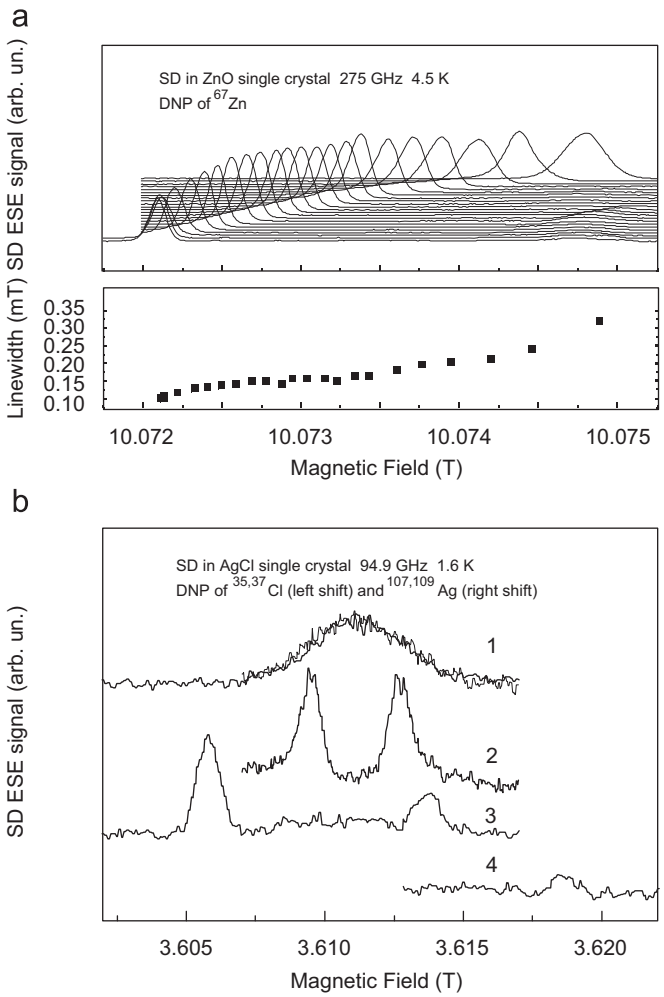

Fig. 1. (a) (top panel) The effect of cw microwave preirradiation on the line position and line shape of the EPR transition at 275 GHz and 4.5 K of the SD in ZnO single crystal. In all curves, the line shape is recorded by detecting the ESE signal by slowly scanning the magnetic field. The curve at the right is the unperturbed line. The first line to the left is recorded after cw microwave irradiation during 2 min at the center of the unperturbed line. The next curve to the left is observed after cw microwave irradiation during 2 min at the center of the second curve to the left, etc. Finally, the line stabilizes at a position shifted by 2.8 mT with respect to the original line position. Simultaneously, the linewidth is reduced from 0.35 to 0.13 mT. (bottom panel) Reduction of the SD linewidth due to DNP. (b) The effect of cw microwave preirradiation on the line position and line shape of the EPR transition at 94.9 GHz and 1.6 K of the shallow donor in AgCl single crystal. The curve at the center (1) is the unperturbed line. The line (2) is observed after cw microwave irradiation during 2 min at the center of the unperturbed line. The next curves (3) and (4) are observed after cw microwave irradiation at the center of the low-magnetic line and high magnetic line, respectively.

the unperturbed ESE-detected EPR line centered at 10.0749 T is displaced by 0.35 mT to the lower field after irradiation with cw microwaves with a power of 1 mW during 120 s at the center of the unperturbed line. Irradiating at the center of this new line position with the same microwave power during the same time again displaces the line to the lower field. When repeating this procedure, the resonance line is finally displaced by 2.8 mT to 10.0721 T with a simultaneous reduction of the linewidth by a factor of 2.5–0.13 mT (Fig. 1(a), bottom panel). Since the line shape of the EPR transition of the shallow H-related donor is determined by the isotropic hf interactions with the nuclear spins of the surrounding ^{67}Zn nuclei, it is obvious that the observed effects are related to a dynamic nuclear polarization process. The microwave irradiation induces an efficient transfer of the large electron-spin polarization caused by the high Boltzmann factor to the ^{67}Zn nuclear-spin system.

The same type of the effect has been discovered in this work in AgCl single crystal. Shallow donors in AgCl are created upon band-to-band optical excitation, and can be studied by EPR at low temperatures. The EPR signals from SD's appear as an isotropic, structureless line at $g = 1.88$ [1]. There are some common properties for SD's in ZnO and AgCl crystals, in both wide-band-gap semiconductors Bohr radius of SD is of about 1.5 nm. Fig. 1(b) shows the effect of cw microwave preirradiation on the line position and line shape of the EPR transition at 94.9 GHz and 1.6 K of the shallow donor in AgCl single crystal. Hole burning, splitting and shifts of the EPR line of the shallow donor in AgCl single crystals have been observed.

The curve at the center (1) is the unperturbed line. The line (2) is observed after cw microwave irradiation during 2 min at the center of the unperturbed line. The next curves (3) and (4) are observed after cw microwave irradiation at the center of the low-magnetic line and high magnetic line, respectively. This effect is caused by a dynamic nuclear polarization process that transfers the almost complete electron-spin polarization to Ag and Cl nuclear spins.

Isotopes ^{107}Ag and ^{109}Ag have the same nuclear spins $I = 1/2$, natural abundance is 51.83%, nuclear g-factor $g_n = -0.2272$ for ^{107}Ag and 48.17% and $g_n = -0.2617$ for ^{109}Ag; for isotopes ^{35}Cl and ^{37}Cl the nuclear spins $I = 3/2$, for ^{35}Cl abundance 51.83%, $g_n = 0.5479$, for ^{37}Cl abundance 48.17% and $g_n = 0.4561$. One can see that nuclear g-factors for Ag and Cl isotopes have different signs, in which connection the sign for Cl is similar to that for the nuclear g factor of ^{67}Zn isotope ($I = 5/2$, 4.1%, $g_n = 0.3503$). Therefore DNP of Cl nuclei seems to result in a shift of the EPR line to a low magnetic field similar to the shift induced by DNP of ^{67}Zn nuclei. In opposite, DNP of Ag nuclei will result in the high-magnetic field shift. It is natural that Ag and Cl nuclei have different relaxation characteristics and different HF interactions with unpaired electron of SD [1]. As a result the splitting of EPR lines has been observed for SD's in AgCl (Fig. 1(b)) which seems to be evoked by a distinction in the DNP effect for different groups of SD's inside of the AgCl crystal.

Fig. 2(a) shows the ESE-detected EPR signals of the SD's in a dry powder of ZnO nanoparticles with a diameter of 2.8 nm observed at a frequency of 94.9 GHz and a temperature of 2 K. Before the EPR experiment ultraviolet light illuminated the sample at 2 K during 30 min to transfer an electron from the surface acceptor in the ZnO nanocrystals to the SD to make the two centers paramagnetic. The lowest curve is recorded without preirradiation. The linewidth 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. The hole and the antihole is

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