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Overhauser Effect of ^{67}Zn Nuclear Spins in ZnO via Cross Relaxation Induced by the Zero-Point Fluctuations of the Phonon Field

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Hole burning in and displacements of the magnetic-resonance absorption line of the electron spin of the shallow hydrogen-related donor in ZnO are observed upon resonant irradiation with microwaves at 275 GHz and at 4.5 K in a magnetic field of 10 T. These effects arise from an almost complete polarization of the many ^{67}Zn ($I = 5/2$) nuclear spins that have an isotropic hyperfine interaction with the electron spin of the shallow donor. It is proposed that this huge dynamic nuclear polarization is caused by a spontaneous-emission-type cross relaxation in the coupled electron-spin nuclear-spin system induced by the zero-point fluctuations of the phonon field.

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Recently, by an electron paramagnetic resonance (EPR) and electron nuclear double resonance (ENDOR) study [1], it was demonstrated that hydrogen acts as a shallow donor in ZnO, thus confirming the observation of muon spin rotation [2] and the prediction of Van de Walle [3]. The experimental evidence was provided by the observation of the ENDOR signals of the nuclear spin of ^1H ($I = 1/2$) in the EPR signal of this shallow donor obtained at 95 GHz. In addition, the ENDOR signals were observed of the ^{67}Zn nuclear spins ($I = 5/2$, abundance 4.1%) that have an isotropic hyperfine (hf) interaction with the unpaired electron spin of the donor. The multitude of ^{67}Zn nuclear-spin resonance lines, showing hf interactions ranging from $a = 2.4$ MHz to $a = 0.01$ MHz, is caused by the fact that the electronic wave function is distributed in the crystal according to a $1s$ -type wave function with a Bohr radius of $15 \text{ \AA}$ [1].

In an annealed ZnO sample, only the EPR signal of the shallow H-related donor is observed. Using our new EPR spectrometer operating at 275 GHz, this EPR signal has a Gaussian line shape with a width of 0.35 mT similar to the width of the resonance line observed at 95 GHz. The linewidth can be simulated by considering the isotropic hyperfine (hf) interaction with the ^{67}Zn nuclear spins as measured in the ENDOR spectrum [1]. The observed Gaussian line shape and linewidth show that the concentration of shallow donors is low and that exchange narrowing, resulting from the overlap of the wave functions of neighboring donors, is negligible.

It appears that the EPR line shape at 275 GHz and 4.5 K depends strongly on preirradiation with resonant microwaves. The upper curve in Fig. 1 shows the Gaussian-shaped electron-spin-echo (ESE) detected EPR line observed without preirradiation. After preirradiation with $\pi/2$ pulses with a duration of 100 ns at a rate of 10^3 s^{-1} during 120 s at a power of 1 mW, it is seen that a hole is burned in the center of the line where the irradiation

took place and that the line is more intense at lower field (curve 0). Curves (3), (6), (9), and (12) recorded 3, 6, 9, and 12 min, respectively, after the preirradiation shows that the hole slowly disappears, but that even after 12 min the original line shape has still not been recovered. Even more remarkable effects are observed after preirradiation

FIG. 1. The effect of pulsed microwave irradiation on the line shape of the EPR transition at 275 GHz and 4.5 K of the shallow H-related donor in ZnO. The magnetic field is perpendicular to the crystal c axis. In all curves, the line shape is recorded by detecting the electron-spin-echo (ESE) signal by slowly scanning the magnetic field. In the upper curve, the EPR line is recorded without preirradiation. The spectrum labeled by (0) is recorded immediately after preirradiation with a series of $\pi/2$ pulses at a rate of 10^3 s^{-1} during 120 s at the center of the line. It is seen that a hole is burned in the center of the line and that in the low-field wing the intensity has increased. Curves (3), (6), (9), and (12) are recorded at 3, 6, 9, and 12 min after the preirradiation, respectively. It is seen that slowly the line shape recovers to its initial unperturbed Gaussian form.

with cw microwaves at the center of the line. In Fig. 2(a), it is seen that 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 to 0.13 mT. Figure 2(b) shows that it takes about 100 min for the shifted line to relax back to its original unperturbed position. During this relaxation, the line first broadens to its original width and then shifts to its starting position.

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 (DNP) process. Apparently, the microwave irradiation induces an efficient transfer of the large electron-spin polarization (Boltzmann factor $\exp\{g_e\beta_e B/kT\} = 180.7$) to the ^{67}Zn nuclear-spin system.

FIG. 2. (a) 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 shallow H-related donor in ZnO. In all curves, the line shape is recorded by ESE detection as in Fig. 1. 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. (b) The recovery of the shifted EPR line back to its original position after 15, 36, 60, and 100 min.

The surprising aspect of the observed DNP is that it occurs for localized electron spins that are not expected to exhibit a rapid modulation of the hf interaction with the nuclear spins as required for an Overhauser effect [4,5]. As yet, in semiconductors the Overhauser effect has been observed only for conduction electrons or for shallow donors at a relatively high concentration ($>10^{16} \text{ cm}^{-3}$) with an exchange interaction that leads to motional averaging of the EPR line [6]. In our case, however, the EPR line of the H donors is inhomogeneously broadened and the ENDOR transitions of the surrounding ^{67}Zn spins can be observed without a sign of exchange averaging, proving that the concentration of donors is so low that the effect of exchange can be ignored.

The common DNP mechanism for localized spins is the solid effect [7,8]. In this solid effect, the transfer of the electron-spin polarization to the nuclear spins is achieved by saturating the forbidden EPR transitions which are weakly allowed by the presence of the dipolar interaction between the electron spins and the nuclear spins. We have saturated these forbidden transitions, which are shifted by ± 27 MHz (the Zeeman frequency of the ^{67}Zn nuclear spins) from the allowed EPR transition, but we could not find any shift of the EPR line caused by a nuclear polarization. We thus exclude that the solid effect can explain our observations.

We propose that in our case the DNP process is an Overhauser effect and that it finds its origin in a direct, spontaneous-emission-type cross relaxation in the electron-spin-nuclear-spin system induced by the zero-point vibrations of the phonon field. In this cross-relaxation process, the electron spin $S = 1/2$ of the shallow donor and the $I = 5/2$ nuclear spin of a ^{67}Zn isotope undergo a simultaneous $\Delta m_S = +1$, $\Delta m_I = -1$ transition. The new aspect is that the modulation of the term $\frac{1}{2}a(r)\{S_+I_- + S_-I_+\}$ of the isotropic hf interaction that induces the cross relaxation is caused by the zero-point vibrations of the phonon field and not by the rapid relative motion of the spins of conduction electrons or by the spins of shallow donors that exhibit an exchange interaction [6]. In the magnetic field of 10 T, the splitting of the electron-spin levels corresponds to 275 GHz and the splitting of the nuclear-spin levels to about 27 MHz. Since at 4.5 K the thermal energy kT is much smaller than the Zeeman splitting of the electron-spin levels which corresponds to 13.2 K, the spin-lattice relaxation is a direct process; i.e., a change of the electron-spin state is accompanied by the creation or the annihilation of a phonon with the same energy [9]. As a result of the large Boltzmann factor at 4.5 K and 10 T, the relaxation rate from the upper to the lower spin manifold is about 20 times faster than the reverse process. In terms of the Einstein A and B coefficients for spontaneous emission and stimulated emission and absorption, the spontaneous-emission relaxation from the upper to the lower electron-spin level, induced by the zero-point vibrations of the

phonon field, dominates. An estimate of this spontaneous-emission-type relaxation rate has been obtained by pulsed EPR experiments from which we find a value of $1.6 \times 10^3 \text{ s}^{-1}$ at 4.5 K. Similarly, an estimate of the spontaneous-emission cross-relaxation rate is derived from the DNP experiments with pulsed and cw preirradiation. In the DNP experiments with pulsed preirradiation, it takes about 120 s at a repetition rate of 10^3 s^{-1} to burn a hole in the EPR line. In the DNP experiments with cw preirradiation, it also takes about 120 s to shift the EPR line. We thus conclude that the spontaneous-emission cross-relaxation rate is about 10^{-2} s^{-1} at 4.5 K, i.e., about 10^5 times slower than the allowed spontaneous-emission relaxation rate. This means that at every excitation of the electron spin the probability is 10^{-5} that during the decay a nuclear spin is flipped. Thus, at an excitation rate of 10^3 s^{-1} it takes 10^2 s to polarize the nuclear spin. Since the nuclear-spin relaxation rate is found to be of the order of 10^{-3} – 10^{-4} s^{-1} , there is hardly any “leakage” and the microwave pumping of the allowed EPR transition leads to an almost complete polarization of the $I = 5/2$ ^{67}Zn nuclear spins in hf contact with the donor electron spin.

The question arises whether the polarization of the ^{67}Zn spins can explain the observed shift of 2.8 mT of the EPR line. To this end, we have performed a numerical calculation of the local field produced by the ^{67}Zn nuclear spins present in the range of the wave function of the shallow donor and polarized in their $m_I = +5/2$ sublevel. In this calculation we assumed the proton to be at an interstitial position between a zinc and oxygen atom [10]. The contribution of the $I = 5/2$ ^{67}Zn nuclear spins in a particular shell with a radius r to the local field was calculated by assuming that the isotropic hf interaction decays proportionally to the density of the electronic wave function, i.e., proportional to $[\exp\{-r/r_0\}]^2$ with $r_0 = 15 \text{ Å}$. Our previous ENDOR experiments [1] tell us that the largest isotropic hf interaction of the ^{67}Zn nuclear spins is about 2.4 MHz. We assign this value to the ^{67}Zn nuclear spins in the first shell at a distance of about 3.5 Å. To calculate the contribution of the more remote ^{67}Zn nuclear spins, we used a quasicontinuous model where the number of Zn atoms in a shell at distance r is taken to be proportional to r^2 . The result of the calculation is presented in Fig. 3 where the local field is plotted as a function of the radius of the sphere containing the polarized ^{67}Zn nuclear spins. The maximum observed shift of 2.8 mT is obtained for a sphere of polarized ^{67}Zn spins with a radius of 20 Å, a value slightly larger than the Bohr radius of the shallow donor wave function. It is gratifying to see that the large shift of the EPR line can be reproduced by this simple calculation. In particular, the finding that the shift is produced by the nuclear spins in a sphere with a radius of the order of the Bohr radius looks reasonable because not only the contribution to the local field of more remote ^{67}Zn spins drops rather quickly but also their cross-relaxation rate, which is proportional to a^2 , slows down considerably.

FIG. 3. The calculated shift of the EPR line of the shallow H-related donor in ZnO induced by the surrounding ^{67}Zn nuclear spins in a sphere with radius r , polarized in their $m_I = +5/2$ sublevel.

The effect on the EPR line of the relaxation of the polarized ^{67}Zn nuclear spins back to their equilibrium value is visible in Fig. 2(b). It is seen that the recovery of the linewidth is faster than the relaxation to the original line position. Apparently, the ^{67}Zn nuclear spins close to the center of the shallow donor wave function, contributing most to the linewidth, relax faster than the remote nuclear spins that contribute more to the overall shift of the line. This finding is in agreement with the contention that the relaxation of the nuclear spin is mainly caused by the modulation of the hf interaction by the relaxation of the electron spin.

The overall features of the nuclear polarization process and the subsequent decay to thermal equilibrium as displayed in Figs. 2(a) and 2(b) can be understood on the basis of an almost complete polarization of the ^{67}Zn spins with a hf interaction with the H-donor electron spin. It is seen, however, that a weak signal remains at the position of the original line during the pumping process. We attribute this phenomenon to incomplete saturation of the EPR line. Apparently, a small fraction of the paramagnetic centers can escape back to the thermal equilibrium position. We think that this incomplete saturation also explains the somewhat complex spectrum that develops during the recovery.

For half-integer paramagnetic spin systems, the one-phonon, spontaneous-emission-type relaxation rate is known to be proportional to ω^5 , where ω is the frequency of the splitting of the electron-spin levels [9]. We thus predict that at 95 GHz in a magnetic field of 3.4 T and at a temperature of 1.6 K where also spontaneous emission dominates, the relaxation rate is slower by a factor of $(275/95)^5 = 203$. In practice, we find that this ratio is 25.

FIG. 4. (a) The EPR line of a shallow donor in a dry powder of ZnO nanoparticles with a diameter of 3.4 nm observed at a frequency of 94.9 GHz and a temperature of 1.5 K. The EPR line has a width of about 9 mT compared to 0.35 mT for the shallow H-related donor in ZnO bulk single crystals as displayed in Fig. 1. The larger linewidth is caused by the anisotropy of the g tensor and the random character of the ZnO nanoparticles. (b) The same EPR line recorded after pre-irradiation with microwaves during 2 min at one position in the EPR line. It is seen that a hole is burned and an antihole develops. These effects are attributed to dynamic nuclear polarization of the ^{67}Zn nuclear spins in the nanocrystals.

We explain this difference by phonon bottlenecking. We think that at 275 GHz the rate of creation of phonons at 275 GHz is so high that these phonons cannot thermalize quickly enough so that the relaxation rate in the spin system slows down. A direct proof of such phonon bottlenecking would be provided by Brillouin scattering from the heated phonon system as demonstrated by Geschwind [11]

In Fig. 4, we present hole burning in the EPR line detected at 95 GHz and at 1.6 K of a shallow donor in nanoparticles of ZnO [diameter 3.4 nm and capped with $\text{Zn}(\text{OH})_2$] indicating that here the ^{67}Zn nuclear spins also become polarized. As yet, the nature of this shallow donor is unclear. The volume of these particles is so small that only 1 out of 10^3 – 10^4 particles is expected to contain a shallow donor. Thus, delocalization of the donor wave function as a result of exchange interactions is excluded suggesting that a DNP process, similar to that in the bulk ZnO material, is causing the polarization of the ^{67}Zn nuclear spins.

In summary, we have observed hole burning in and shifts of the EPR line of the shallow H-related donor in bulk ZnO single crystals at 275 GHz and 4.5 K upon prolonged resonant irradiation of the EPR transition. This effect is caused by a dynamic nuclear polarization process that transfers the almost complete electron-spin polarization to the ^{67}Zn ($I = 5/2$) nuclear spins. The mechanism responsible for this transfer is a cross relaxa-

tion induced by a modulation of the isotropic hf interaction of the electron spin and the surrounding ^{67}Zn nuclear spins. We propose that the modulation of this hf interaction is caused by the zero-point fluctuations of the phonon field. The DNP effect is so large because the starting electron-spin polarization is almost complete ($>95\%$), because spontaneous-emission decay induced by the zero-point fluctuations of the phonon field dominates the relaxation process and because the intrinsic nuclear-spin relaxation rate is very slow. Thus, the observed dynamic nuclear polarization mechanism is essentially an Overhauser effect. The remarkable aspect is that the effect occurs in a localized paramagnetic spin system in a solid, whereas it is usually assumed that the Overhauser effect occurs for electron and nuclear systems that exhibit a rapid relative movement. In addition, we report dynamic nuclear polarization effects in ZnO nanoparticles that seem to be caused by a similar mechanism.

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