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Light-induced nuclear quadrupolar relaxation in semiconductors

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Light excitation of a semiconductor, known to dynamically polarize the nuclear spins by hyperfine contact interaction with the photoelectrons, also generates an intrinsic nuclear *depolarization* mechanism. This relaxation process arises from the modulation of the nuclear quadrupolar Hamiltonian by photoelectron trapping and recombination at nearby localized states. For nuclei near shallow donors, the usual diffusion radius is replaced by a smaller, quadrupolar, radius. If the light excitation conditions correspond to partial donor occupancy by photoelectrons, the nuclear field experienced by electrons trapped at shallow donors can be decreased by more than 1 order of magnitude.

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I. INTRODUCTION

In a semiconductor, the possibility to enhance the nuclear polarization by the hyperfine contact interaction with spin-polarized electrons generated by circularly polarized light excitation is of interest both for fundamental reasons and, among others, for applications to (i) quantum computing,[1] (ii) transfer of nuclear magnetization to biological systems, as an alternative to adsorption of polarized xenon,[2,3] and (iii) understanding of the fractional quantum Hall effect.[4] Further potential applications of the optical increase of NMR sensitivity include extension to nuclei of *single spin* investigations using magnetic-resonance force microscopy at surfaces.[5]

After the demonstration of optical nuclear polarization in silicon,[6] a number of recent investigations of the optically enhanced *bulk* nuclear magnetization have been undertaken using standard NMR in Si,[7] GaAs,[8–13] InP,[14] and CdTe.[15] Some of the results[11–13] were used to verify the predictions of a general theory for nuclear relaxation in solids according to which the presence of paramagnetic impurities, or localized centers, is crucial for relaxation of the nuclear-spin system.[16–18] Nuclei close to the centers are relaxed by the hyperfine interaction with the spin-polarized photoelectrons trapped at these impurities, while the bulk nuclear-spin system is relaxed by spin diffusion from the latter minority nuclei. A diffusion radius is defined corresponding to the distance from the impurity separating the two types of relaxation processes.[19]

Optical detection of NMR, from the depolarization at resonance of the luminescence, was first reported for GaAlAs in 1974 (Ref. 20) and subsequently applied to several III-V semiconductors,[21–24] as well as two-dimensional systems[8,25] and quantum dots.[26,27] For bulk materials, this technique was shown to only detect nuclei near the sites of electronic localization, which verifies the existence of a diffusion radius.[28] The ratio of the nuclear hyperfine field acting on the electrons and of the optically measured electronic spin polarization is consistently smaller than its calculated value. The corresponding reductions of the nuclear field are found to be of 0.1 for GaAs,[29] 0.02 for GaSb,[22] and of several percent for InP.[23] Such decreases are likely to significantly reduce the optical enhancement of the nuclear polarization.

The identification of the relaxation mechanisms responsible for this loss of nuclear polarization remains an open problem. In the absence of light excitation, the hyperfine coupling with the unpolarized holes[30] or the quadrupolar interaction modulated by lattice phonons[31] is negligible at low temperature. The total hyperfine field of nuclei near shallow donors is decreased because of the competition between spin-lattice relaxation and spin diffusion, but only by a factor 3.[28] Another possibility is that the averaging caused by spin exchange between trapped electrons and free electrons reduces the effective nuclear field measured experimentally.[21] Interestingly, in addition to the dynamic nuclear polarization, light excitation also creates an *intrinsic leakage mechanism* for the same nuclei as the ones which are dynamically polarized. The nuclei close to shallow donors experience a very strong electric field from the ionized donor. Since the latter field is modulated by trapping and recombination of photoelectrons, there results a significant nuclear depolarization.

The present work is devoted to an evaluation of the efficiency of such light-induced nuclear relaxation for the case of nuclei near shallow donors. In Sec. II, the characteristic time of the quadrupolar-induced evolution of the nuclear-spin temperature is calculated using the semiclassical rate equation for the nuclear-spin-density matrix.[32] Quantitative estimates of the nuclear magnetization as a function of distance to the donor and of the nuclear field experienced by electrons trapped at shallow donors are performed in Sec. III using the known magnitudes of quadrupolar[33–36] and hyperfine couplings.[29] Provided the light power density is such that shallow donors are partially occupied, the light-induced quadrupolar relaxation is found to induce a decrease of the nuclear hyperfine field by as much as 1 order of magnitude. The corresponding effect in quantum dots and the resulting dependence of the nuclear field as a function of temperature and light excitation power will be discussed elsewhere.[37]

II. LIGHT-INDUCED QUADRUPOLAR NUCLEAR RELAXATION TIME AND NUCLEAR POLARIZATION VALUE

In the absence of a trapped photoelectron, the electric field experienced by nuclei near a shallow donor is given by

$$E_{\text{off}}(r) = \frac{|e|}{4\pi\varepsilon\varepsilon_0} \cdot \frac{1}{r^2}, \tag{1}$$

where e is the electronic charge, ε is the static dielectric constant, and r is the distance from the donor. Photoelectron trapping and recombination induce a modulation of the electric field between Eq. (1) and $E_{\text{on}}(r)$ such that

$$E_{\text{on}}(r) = E_{\text{off}}(r)[1 - s(r)], \tag{2}$$

where the expression for $s(r)$, found using Gauss's theorem and the shape of the electronic wave function, is

$$s(r) = 1 - \left[1 + \frac{2r}{a_0^*} + \frac{2r^2}{a_0^{*2}}\right] e^{-2r/a_0^*}. \tag{3}$$

Here a_0^* is the electronic Bohr radius. One has $s(a_0^*) \approx 0.3$ and, in GaAs, $E_{\text{off}}(a_0^*)$ is of the order of 10^6 V/m. The modulation amplitude $E_{\text{off}}(r) - E_{\text{on}}(r)$ induced by photoelectron trapping and recombination is very large. Unlike the usual quadrupolar relaxation, the corresponding relaxation process does not rely on phonons for modulation and can be relevant at low temperature. The present section is devoted to the calculation of the corresponding relaxation time and of the resulting decrease of the nuclear polarization.

TABLE I. The quantity b_Q, which has the dimension of the ratio of a magnetic field to an electric field, is given by Eq. (7) and characterizes the strength of the quadrupolar relaxation. This quantity estimated in Appendix A is given below for several nucleus and/or semiconductor matrix combinations. Also shown are estimated values of the antishielding factor R_{14}, defined by Eq. (7).

Nucleus	$R_{14}(10^{12}\ \text{m}^{-1})$	$b_Q(10^{-10}\ \text{Tm/V})$
GaAs^{75}	3.2	2.8
Ga^{69}As	2.8	2.0
Ga^{71}As	2.8	1.9
In^{115}As	4.4	0.7
InAs^{75}	1.9	1.6
Ga^{69}Sb	0.7	0.51
GaSb^{121}	1.9	1.2
In^{115}P	~4	~0.60

A. Quadrupolar Hamiltonian

The nuclear-spin Hamiltonian, given by $H = Z + H_{\text{IS}} + H_{\text{SS}} + H_Q$, is the sum of the Zeeman term Z, of the hyperfine Hamiltonian H_{IS}, of the nuclear-spin-spin interaction H_{SS}, and of the quadrupolar interaction H_Q. The expressions for the first three terms can be found in Ref. 29. For a cubic semiconductor, the expression for the quadrupolar Hamiltonian is given in Appendix A for arbitrary magnetic field B and sample surface orientations. If the magnetic field is perpendicular to a (001) sample surface, which is the case of a wide majority of experimental situations, the quadrupolar Hamiltonian is simpler,

$$H_Q = F_Q(r) \sum_{k=1}^{2} [A_{Qk} + A_{Qk}^+]. \tag{4}$$

Taking the normal z to the surface as the quantization axis, the spin operators A_{Qk} are given by

$$A_{Q1} = \sin\,\theta e^{i(\phi - \pi/2)}[I_z I_+ + I_+ I_z],$$

$$A_{Q2} = -i\cos\,\theta I_+^2, \tag{5}$$

and the Hermitian conjugate operators A_{Qk}^+ are obtained by replacing i by $-i$ and therefore I_+ by I_-. Here θ is the angle between z and the direction Z of the electric field $\vec{E}$ and φ is the angle between the x direction and the zZ plane. The operators A_{Qk} induce transitions between Zeeman spin levels separated by energies given by

$$\hbar\omega_k = k\hbar\gamma B \quad (k = 1,2), \tag{6}$$

where γ is the nuclear gyromagnetic ratio. It is convenient to write[38,39]

$$F_Q(r) = \frac{eR_{14}Q}{4I(2I-1)} E(r) = \hbar\gamma b_Q E(r), \tag{7}$$

where e is the electronic charge and Q is the quadrupolar moment of the bare nucleus of spin I. The factor R_{14}, which includes the electrostatic antishielding, is in the present frame of coordinates Oxyz, the value of the only nonzero components of the third rank tensor relating the electric-field gradient to the electric field.[33–36] The quantity $b_Q = eR_{14}Q[4\hbar\gamma I(2I-1)]^{-1}$ is the ratio of a magnetic to an electric field. It is calculated in Appendix A for different compounds and is given in Table I. The Hamiltonian H_Q can be rewritten as the sum of a static and of a modulated part,

$$H_Q = [1 + h(t)]F_{0Q}(r) \sum (A_{Qk} + A_{Qk}^+), \tag{8}$$

where $F_{0Q}(r)$ is given by

$$F_{0Q}(r) = [1 - s(r)\Gamma_t]F_{Q\ \text{off}}(r) = \hbar\gamma[1 - s(r)\Gamma_t]b_Q E_{\text{off}}(r) \tag{9}$$

and Γ_t is the fraction of the time during which the electron is present at the donor site. The function $h(t)$ describes temporal fluctuations due to the trapping and recombination of an electron at the localized site. This function has a time average equal to zero and varies randomly between $s(r)\Gamma_t[1 - s(r)\Gamma_t]^{-1}$ and $-s(r)(1-\Gamma_t)[1 - s(r)\Gamma_t]^{-1}$. Its correlation function, as found in Appendix B, is given by

$$g(\tau) = \langle h(t)h(t-\tau)\rangle = \frac{\Gamma_t(1-\Gamma_t)s(r)^2}{[1 - s(r)\Gamma_t]^2} e^{-|\tau|/\tau_{cQ}}. \tag{10}$$

The latter result expresses the fact that the interaction is not modulated for $s=0$ or $\Gamma_t=0$ or $\Gamma_t=1$. The correlation time τ_{cQ} for the quadrupolar interaction is the sum of two independent contributions,

$$1/\tau_{cQ} = 1/\tau_r + 1/\tau_c, \tag{11}$$

where τ_r is the recombination time of the electron trapped at the donor and τ_c is the lifetime of the ionized donor due to capture of a free electron.

B. Calculation of the nuclear relaxation time

Following a semiclassical treatment, the quadrupolar-induced evolution of the nuclear-spin-density matrix σ^* for the nuclear-spin system, in the interaction representation and within the secular approximation, is given by[32]

$$\left.\frac{d\sigma^*}{dt}\right|_Q = -\frac{i}{\hbar}[H_0,\sigma^*] - \frac{[F_{0Q}(r)]^2}{\hbar^2} \times \sum_k [A_{Qk},[A^+_{Qk},\sigma^* - \sigma_0]]J_Q(\omega_k), \qquad (12)$$

where H_0 is the total static Hamiltonian and σ_0 is the steady-state value of σ^*. The spectral density function $J_Q(\omega_k)$, taken for ω_k defined by Eq. (6), is given by[40]

$$J_Q(\omega_k) = \int_{-\infty}^{+\infty} e^{-i\omega_k\tau} g(\tau)d\tau. \qquad (13)$$

Here, we assume that the existence of interactions between nuclei results in the establishment of a temperature among the nuclear-spin system. With the latter hypothesis, justified in Sec. III D, the nuclear-spin-density matrix is, in the high-temperature limit, of the form[29]

$$\sigma \approx [1 - \beta(Z + H_{\mathrm{IS}} + H_Q + H_{\mathrm{SS}})]/\mathrm{Tr}(1) \qquad (14)$$

where $\beta = 1/k_B T_n$, k_B is the Boltzmann constant and T_n is the temperature of the nuclear-spin system. It is then found that the nuclear mean spin lies along the direction of the magnetic field independently of the relative magnitudes of Zeeman and quadrupolar interactions.

Since the latter operator σ commutes with the static Hamiltonian, the density matrix in the interaction representation is $\sigma^* = \sigma$ and also the first term of Eq. (12) vanishes. An equation for evolution of the inverse nuclear-spin temperature β is obtained, after multiplication of Eq. (12) by I_z, taking the trace, and using Eq. (14). Assuming that $\sigma \approx (1 - \beta Z)/\mathrm{Tr}(1)$ (these large magnetic-field conditions are defined more precisely in Sec. III D), one obtains

$$\left.\frac{\partial\beta}{\partial t}\right|_Q = -\frac{1}{\hbar^2}[F_{0Q}(r)s(r)]^2 \frac{\Gamma_t(1-\Gamma_t)}{[1 - s(r)\Gamma_t]^2}\left[\sum_k \frac{2K_k(\theta)\tau_{cQ}}{1 + \omega_k^2\tau_{cQ}^2}\right] \times (\beta - \beta_L). \qquad (15)$$

Here $\beta_L = 1/k_B T_L$, with T_L being the temperature of the lattice. The numerical, angle-dependent, quantity $K_k(\theta)$, defined by

$$K_k(\theta) = \mathrm{Tr}\{I_z[A_{Qk},[A^+_{Qk},I_z]]\}/\mathrm{Tr}[I_z^2], \qquad (16)$$

is calculated in Appendix C. Its value is as expected zero for $I = \frac{1}{2}$ and is given by

$$K_1(\theta) = \frac{2}{5}[4I(I+1) - 3]\frac{E^2_{\mathrm{off}\,\perp}(r,\theta)}{E^2_{\mathrm{off}}(r)}, \qquad (17)$$

$$K_1(\theta) + K_2(\theta) = \frac{2}{5}[4I(I+1) - 3]\left[1 + 3\frac{E^2_{\mathrm{off}\,\parallel}(r,\theta)}{E^2_{\mathrm{off}}(r)}\right], \qquad (18)$$

where we recall that the parallel and perpendicular components of the electric field, defined with respect to the normal z to the surface, are equal to $E_{\mathrm{off}} \cos\theta$ and $E_{\mathrm{off}} \sin\theta$, respectively. The quadrupolar relaxation rate is finally given by

$$\frac{1}{T_{1Q}(r,\theta)} = \Gamma_t(1-\Gamma_t)\{\gamma b_Q[E_{\mathrm{off}}(r) - E_{\mathrm{on}}(r)]\}^2\left[\frac{2K_1(\theta)\tau_{cQ}}{1 + \omega_1^2\tau_{cQ}^2} + \frac{2K_2(\theta)\tau_{cQ}}{1 + \omega_2^2\tau_{cQ}^2}\right]. \qquad (19)$$

Its value is proportional to the square of the amplitude of the modulated electric field and further depends on the angle θ which defines the direction of the electric field.

C. Steady-state nuclear mean spin

The rate equation for the evolution of the nuclear mean spin along z, neglecting the thermodynamic nuclear and electronic polarizations in the applied magnetic field as well as nuclear-spin-lattice relaxation processes other than the hyperfine and quadrupolar ones, is given by

$$\frac{d\langle I_z(r,\theta)\rangle}{dt} = -\frac{1}{T_{1H}(r)}\left(\langle I_z(r,\theta)\rangle - \frac{4}{3}[I(I+1)]\langle S_z\rangle\right) - \frac{1}{T_{1Q}(r,\theta)}\langle I_z(r,\theta)\rangle + D\Delta\langle I_z(r,\theta)\rangle, \qquad (20)$$

where $T_{1H}(\vec{r})$ is the relaxation time due to the hyperfine coupling and $\langle S_z\rangle$ is the mean electronic spin along the direction z of light excitation. The third term of the latter equation describes spin diffusion due to flip-flops between neighboring spins.[10,16–18,28] Here Δ is the Laplacian operator and D is the diffusion constant. Throughout the present work, it will be considered that the duration of light excitation, although sufficient to polarize the nuclei close to the donor by spin-lattice relaxation, is too short to allow this polarization to be transferred to the bulk nuclei by spin diffusion. As will be shown in Sec. III C, in the latter case, spin diffusion only marginally modifies the results of the present section so that this term will not be considered here. The steady-state value of the nuclear mean spin under the sole effect of spin-lattice relaxation is given by

$$\langle I_z(r,\theta)\rangle = p(r,\theta)\frac{4}{3}[I(I+1)]\langle S_z\rangle = \frac{4}{3}\frac{f(r,\theta)}{1 + f(r,\theta)}[I(I+1)]\langle S_z\rangle, \qquad (21)$$

where $0 < p(r,\theta) < 1$ expresses the reduction of nuclear mean spin with respect to its maximum value $\frac{4}{3}[I(I+1)]\langle S_z\rangle$. The quantity $f(r,\theta)$, given by

$$f(r,\theta)=\frac{T_{1Q}(r,\theta)}{T_{1H}(r)}, \tag{22}$$

is equal to $p(r,\theta)$ in the extreme case where the quadrupolar relaxation is much more efficient than the hyperfine one. The relaxation time $T_{1H}(r)$ is given by[28]

$$\frac{1}{T_{1H}(r)}=\Gamma_t[\gamma b_e^*(r)]^2\frac{2\tau_{cH}}{1+\omega_H^2\tau_{cH}^2}. \tag{23}$$

Here, $b_e^*(r)$ is the *instant* electronic hyperfine field acting on the nuclei. The time τ_{cH} is the correlation time of the hyperfine interaction. The energy $\hbar\omega_H$, corresponding to the flip-flop of an electronic and a nuclear spin, is given by

$$\hbar\omega_H \approx \hbar\gamma_e(B\pm B_n), \tag{24}$$

where B_n is the nuclear hyperfine field acting on the electrons, which is added or subtracted to B depending on the sign of the electronic spin. The latter energy, which depends on the *electronic* gyromagnetic ratio γ_e, is larger than $\hbar\omega_1$ and $\hbar\omega_2$ by about 3 orders of magnitude.

Assuming that $\omega_H^2\tau_{cH}^2$, $\omega_1^2\tau_{cQ}^2$, and $\omega_2^2\tau_{cQ}^2$ are small with respect to unity, which sets an upper limit to the magnetic-field value, the quantity $f(r,\theta)$ is finally given by

$$f(r,\theta)\approx\frac{\tau_{cH}}{\tau_{cQ}}\cdot\frac{1}{(1-\Gamma_t)}\left[\frac{b_e^*(r)}{b_Q[E_{\text{off}}(r)-E_{\text{on}}(r)]}\right]^2[\Sigma_k K_k(\theta)]^{-1}. \tag{25}$$

Note that, since the spatial dependence of the electric fields $E_{\text{off}}(r)$ and $E_{\text{on}}(r)$ does not appear explicitly, Eqs. (19) and (25) are valid for any localized electronic state. For nuclei near a donor one has

$$b_Q E_{\text{off}}(r)=b_Q E_{\text{off}}(a_0^*)(a_0^*/r)^2, \tag{26}$$

$$b_e^*(r)=b_e^*(a_0^*)e^{-2(r/a_0^*-1)}. \tag{27}$$

Using Eqs. (2) and (18), it is possible to separate $f(r,\theta)$ into the product of a radial dependence $\phi(r)$, of an angular one, and of a numerical coefficient f_0, which are measures of the relative strengths of hyperfine to quadrupolar relaxations,

$$f(r,\theta)\approx\frac{f_0\varphi(r)}{1+3\cos^2\theta}, \tag{28}$$

$$\varphi(r)=\frac{e^{-4(r/a_0^*-1)}}{s(r)^2}\left(\frac{r}{a_0^*}\right)^4, \tag{29}$$

$$f_0=\frac{5}{2}[4I(I+1)-3]^{-1}(1-\Gamma_t)^{-1}\frac{\tau_{cH}}{\tau_{cQ}}\left(\frac{b_e^*(a_0^*)}{b_Q E_{\text{off}}(a_0^*)}\right)^2. \tag{30}$$

The implications of the latter equations are discussed in Sec. III.

III. DISCUSSION

A. Effect of the donor rate of occupation

A key parameter for the value of f_0 is the rate of occupation of the donors Γ_t by photoelectrons, which depends on the light excitation power.

(a) The correlation times τ_{cH} and τ_{cQ} depend on the free-electron density n_f. The time τ_{cQ} can be written using Eq. (11),

$$\frac{1}{\tau_{cQ}}=\frac{1}{\tau_r}+\sigma_c v n_f, \tag{31}$$

where v is the velocity of free electrons and σ_c is the cross section for their capture at donors. The correlation time τ_{cH} of the hyperfine interaction is given by

$$\frac{1}{\tau_{cH}}=\frac{1}{2\tau_r}+\frac{1}{T_1}+\frac{1}{\tau_{\text{ex}}}\approx\sigma_e v n_f \tag{32}$$

as obtained in Appendix B, assuming that the electronic polarization is weak with respect to unity. Here T_1 is the electronic spin—lattice relaxation time and τ_{ex} are the characteristic times for spin exchange between trapped and free electrons. In GaAs, for above band-gap light excitation, it has been found that the latter process is dominant by several orders of magnitude, so that τ_{cH} has a simple approximate expression, also given in Eq. (32), where σ_e is the spin-exchange cross section.[21]

(b) The rate Γ_t of donor occupation is obtained by writing the rate equation for the population of electrons trapped at donors of concentration N_D. The latter equation, given in Appendix D considering above band-gap light excitation, yields

$$\Gamma_t=\frac{\sigma_c\tau_r v n_f}{1+\sigma_c\tau_r v n_f}. \tag{33}$$

Using Eqs. (28)–(30), f_0 is given by

$$\begin{aligned} f_0&=\frac{5}{2}\frac{\sigma_c}{\sigma_e}[4I(I+1)-3]^{-1}\left(\frac{b_e^*(a_0^*)}{b_Q E_{\text{off}}(a_0^*)}\right)^2\frac{1}{\Gamma_t(1-\Gamma_t)}\\ &=\frac{f_{00}}{\Gamma_t(1-\Gamma_t)}. \end{aligned} \tag{34}$$

Equation (34) has a simple form in which the quantity f_{00}, which is a measure of the maximum magnitude of the quadrupolar-induced loss of nuclear magnetization, is independent of experimental conditions such as excitation power. The latter dependence is concentrated in the donor occupation rate Γ_t. According to Eq. (34), the quadrupolar-induced loss of nuclear polarization occurs when the donors are *partially* occupied, which can be easily characterized from the power dependence of the donor luminescence. For a density of conduction electrons much smaller than $(\sigma_c\tau_r v)^{-1}$, one has $\Gamma_t \ll 1$ and the quadrupolar effects are small since the correlation time t_{cH} is large. Conversely, if $\Gamma_t=1$, the quadrupolar interaction is not modulated and cannot relax the nuclear spins.

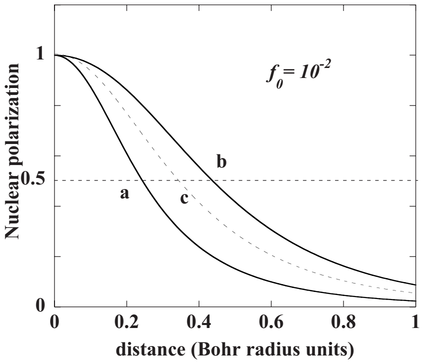

FIG. 1. Dependence of the normalized nuclear polarization, defined by Eq. (21), (a) along the magnetic-field direction and (b) along the perpendicular direction, as a function of distance to the donor. Also shown is the radial dependence of the angular average of the nuclear polarization, defined by Eq. (35). The relative magnitude f_0 of hyperfine and quadrupolar relaxations, given by Eq. (30), is taken as equal to 10^{-2}. The distance at which the magnetization is equal to 0.5 is of (a) $0.25a_0^*$ in the direction of the magnetic field, (b) $0.45a_0^*$ in the perpendicular direction, and (c) $\rho_Q=0.35a_0^*$ after angular averaging.

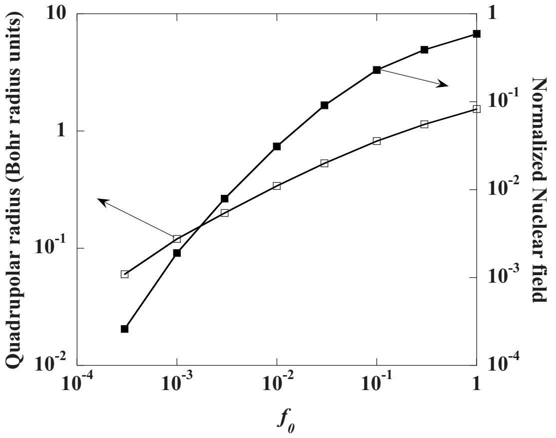

FIG. 2. Dependence of the quadrupolar radius ρ_Q and of $s(\rho_Q)$, which expresses the quadrupolar-induced nuclear field decrease, on the relative magnitude f_0 of hyperfine and quadrupolar relaxations. If no light-induced quadrupolar relaxation is present, the quadrupolar radius is replaced by the usual diffusion radius ρ_D,of the order of the Bohr radius. For $f_0=10^{-2}$, the quadrupolar radius is $0.35a_0^*$, and the nuclear field is further decreased by about 1 order of magnitude.

B. Order of magnitude estimates

For As^{75} in GaAs, the efficiency of the quadrupolar relaxation process comes from the fact that the spin-exchange cross section [$\sigma_e \sim 9\times 10^{-16}$ m^2] (Ref. 21) is 3 orders of magnitude larger than the one for electron capture at donors [$\sigma_c=5.1\times 10^{-19}$ m^2].[41] Using Table I and Ref. 29, we obtain $b_e^*(a_0^*)=1.5$ mT$\approx 5.2 b_Q E_{\mathrm{off}}(a_0^*)$ and we find $f_{00}\sim 2\times 10^{-3}$ and $f_0\sim 10^{-2}$ for $\Gamma_t=1/2$. As found from Eq. (28), $f(a_0^*,\pi/2)\approx 10^{-1}$ and $f(a_0^*,0)\approx 2\times 10^{-2}$, so that the nuclei at the Bohr radius are depolarized by the quadrupolar relaxation.

Nuclei such as In^{115} in InP and Sb^{121} in GaSb are believed to exhibit stronger quadrupolar effects because of their larger spin values (9/2 for In^{115} and 5/2 for Sb^{121}). However, as seen in Table I, the quantity b_Q is smaller than for As^{75} in GaAs. Using Table I and Eq. (34) and assuming that both σ_c and σ_e scale like the Bohr radius, so that their ratio is independent on material, we estimate that f_{00} is equal to 9.4×10^{-3} and 1.2×10^{-2} for In^{115} in InP and Sb^{121} in GaSb, respectively. This implies that the latter materials should also exhibit nuclear polarization losses of quadrupolar origin, although slightly smaller than for GaAs.

C. Radial and angular dependences of the nuclear polarization: Quadrupolar diffusion radius

Shown in Fig. 1 are the radial dependences of $p(r,0)$ and $p(r,\pi/2)$ using $f_0\sim 10^{-2}$. Close to the donor position, one has $p(r,\theta)=1$, as the quadrupolar relaxation is inefficient because $s(r)\approx \frac{4}{3}(r/a_0^*)^3$ so that the electric field is not modulated. As a function of distance, although the quadrupolar rate first increases and then decreases, $f(r,\theta)$ exhibits a monotonic, decreasing behavior. The nuclei are depolarized above a distance to the donor corresponding to $f=1$. As seen in Fig. 1, this distance is smaller in the direction z of the magnetic field ($0.25a_0^*$) than in the perpendicular directions ($0.45a_0^*$).

For calculation of the nuclear field experienced by trapped electrons, two approximations will be made. First, we shall use for simplicity the *angular* average of the nuclear polarization, defined as $\langle p(r)\rangle=\int \sin\theta p(r,\theta)d\theta d\varphi/\int \sin\theta d\theta d\varphi$. As found using Eqs. (21) and (28), this quantity is given by

$$\langle p(r)\rangle = \frac{f_0\varphi(r)}{\sqrt{3[1+f_0\varphi(r)]}}\mathrm{arctg}\left[\frac{\sqrt{3}}{\sqrt{1+f_0\varphi(r)}}\right] \qquad (35)$$

for which the radial dependence, also shown in Fig. 1, is intermediate between those of $p(r,0)$ and $p(r,\pi/2)$. The second approximation consists in replacing $\langle p(r)\rangle$ by a step function at $r=\rho_Q$ such that

$$\langle p(\rho_Q)\rangle = \frac{1}{2}. \qquad (36)$$

The nuclear hyperfine field, defined by $B_n=4B_{n0}a_0^{*-3}\int_0^\infty r^2 e^{-2r/a_0^*}\langle p(r)\rangle dr$,[29] is approximated by

$$B_n \approx B_{n0}s(\rho_Q), \qquad (37)$$

where B_{n0} is the nuclear field value for a homogeneous nuclear polarization and $s(r)$ is defined in Eq. (3). The latter approximation implies that the quadrupolar relaxation is inefficient for distances smaller than ρ_Q and dominant for larger distances ($f=0$). Such approximation is usual in analyses of nuclear polarizations near shallow donors[16–18] and results in defining a sphere around the donor inside which the nuclear polarization is not affected by the quadrupolar relaxation. The radius of this sphere, which will be called the quadrupolar radius, replaces the usual diffusion radius for the estimate of the nuclear hyperfine field. Shown in Fig. 2 are the variations of ρ_Q and of $s(\rho_Q)$, as a function of f_0. For $f_0=10^{-2}$, one finds $\rho_Q\sim 0.35a_0^*$ which leads to $B_n=0.03B_{n0}$.

We now discuss the effect of spin diffusion between neighboring spins, which appears as the third term of Eq. (20) and has so far been neglected. A diffusion radius ρ_D is defined, corresponding to the distance from the donor at which the efficiencies of direct relaxation and of spin diffusion are equal. This radius is given by

$$\frac{1}{T_{1Q}(\rho_D)}+\frac{1}{T_{1H}(\rho_D)}=\frac{D}{\rho_D^2}. \tag{38}$$

At a distance smaller than ρ_D, all the considerations of the present work are valid, since spin diffusion does not affect the nuclear polarization. On the other hand, for nuclei situated beyond ρ_D, the polarization is strongly decreased because of the efficient diffusion toward the bulk nuclei. In the absence of quadrupolar relaxation, the maximum value of the reduced nuclear field is $s(\rho_D)$. Since a value $\rho_D \sim 1.4a_0^*$ has been found,[28] we obtain $s(\rho_D)\sim 0.5$. As seen from Eq. (38), the quadrupolar relaxation results in a decrease of ρ_D. For $f_0=10^{-2}$ and using the value of D of Ref. 28, we calculate a modified diffusion radius ρ_D value close to a_0^*. Since the latter value is still larger than ρ_Q, spin diffusion is generally negligible with respect to spin-lattice relaxation for the nuclei which contribute to the nuclear field experienced by trapped electrons.[42]

Spin diffusion should, however, be taken account of into two extreme cases concerning the light excitation power. In the case of a very weak efficiency of the overall spin-lattice relaxation, Eq. (38) does not have a real solution so that spin diffusion becomes predominant at all distances from the donor. Since the efficiencies of both the hyperfine and quadrupolar relaxation processes are proportional to Γ_t, such case is obtained for a weak light excitation density. (For As^{75} in GaAs, we estimate that this situation corresponds to a threshold characterized by $\Gamma_t<0.15$.) This situation is outside the scope of the present work and is not considered here. Conversely, for a high light excitation power, if $\Gamma_t\sim 1$, the quadrupolar radius ρ_Q increases because the quadrupolar spin-lattice relaxation becomes negligible with respect to the hyperfine one. When ρ_Q is larger than ρ_D, since the polarization of nuclei at a distance larger than ρ_D is decreased by spin diffusion toward the bulk nuclei, the nuclear field is obtained by replacing ρ_Q by ρ_D in Eq. (37). Thus, the maximum nuclear field obtained for a negligible quadrupolar relaxation is given by $B_{n0}s(\rho_D)$. As a result, the relative decrease of the nuclear field produced by the light-induced quadrupolar relaxation is $s(\rho_D)/s(\rho_Q)$ which, in the conditions of Fig. 1, is of the order of 15.

D. Magnetic field effects

The present section is devoted to the justification of three hypothesis made in Sec. II B, for which the validity depends on the magnetic-field value.

(1) The zero magnetic-field expression of the quadrupolar-induced decrease of nuclear magnetization has been used in Eq. (25). With the values of the cross sections σ_c and σ_e given in Sec. III B and taking $n_f=10^{21}$ m^{-3}, one finds that $\omega_H\tau_{cH}=1$ for $B=20$ T. The same magnetic-field value gives $\omega_1\tau_{cQ}=1$, further taking $\tau_r\sim 1$ ns.[43] It is concluded that Eq. (25) is valid up to very large magnetic-field values.

(2) It has been assumed that the heat capacity of the Zeeman reservoir is larger than those of the quadrupolar and spin-spin ones. Such assumption is obviously not valid at very low magnetic field. The lower magnetic-field limit is obtained by expressing the heat capacities of the various reservoirs using the following relation:[29]

$$\frac{\langle Z\rangle}{B^2}=\frac{\langle H_{SS}\rangle+\langle H_Q\rangle}{B_L^2+B_Q^2}=-\frac{1}{k_BT_n}\frac{I(I+1)}{3}(\gamma\hbar)^2, \tag{39}$$

where the electronic field acting on the nuclear spins has been neglected. Here B_L is the local field. For a magnetic field larger than B_L, only flip-flops between nuclei of the same isotopic species are energetically allowed. In the particular case of As^{75} in GaAs, this leads to $B_L\sim 0.03$ mT.[29] The local field of quadrupolar origin B_Q, equal to zero for $I=\frac{1}{2}$, is given by

$$\begin{aligned}B_Q^2&=\frac{3\ \mathrm{Tr}\langle H_Q^2\rangle}{I(I+1)(2I+1)(\gamma\hbar)^2}\\&=\frac{4}{5}(b_QE_{\mathrm{off}})^2(1-s\Gamma_t)^2[4I(I+1)-3].\end{aligned} \tag{40}$$

We conclude that the high-field limit discussed in Sec. II B is valid provided

$$B^2 \gg B_L^2+B_Q^2. \tag{41}$$

Thus, the *effective* local field is larger than the spin-spin local field. For a magnetic field along the z direction, assuming for simplicity $\Gamma_t=0$ and taking $r\approx 0.5a_0^*$, we calculate $B_Q\sim 1.6$ mT which is more than 1 order of magnitude larger than B_L.

(3) The hypothesis made in Sec. II B of a nuclear-spin temperature gives an independent low magnetic-field limit for the validity of the present model. In the absence of quadrupolar couplings, there is no doubt that there exists a spin temperature since the time T_2 of establishment of the nuclear temperature is of the order of $1/\gamma B_L\sim 300$ μs. The inclusion of quadrupolar interactions does not change the latter picture provided the following condition is fulfilled:

$$\Delta E=|[\delta_QE_m^i-\delta_QE_{m-1}^i]-[\delta_QE_{m'+1}^j-\delta_QE_{m'}^j]|<\hbar\gamma B_L, \tag{42}$$

where ΔE is the energy balance of a difference between transition energies, expressed as a function of the quadrupolar-induced shift $\delta_QE_m^i$ of the level m of spin i. Here, j is the nearest neighbor of nucleus i of the same isotopic specie. There are two distinct reasons for which the latter condition is likely not to be fulfilled.

(i) For a *homogeneous* electric field, although the quadrupolar shifts of nuclei i and j are the same, one has $\delta_QE_m^i\neq\delta_QE_{m'}^j$, for $m\neq m'$. This may prevent some flip-flops between neighboring nuclei and therefore induce a decrease of the local field. Following Abragam,[44] it is found that such effect leads to a decrease by only 15%, so that quadrupolar interactions weakly affect the time T_2 of establishment of a nuclear-spin temperature.

(ii) Near a donor, flip-flops between nearest neighbors may be prohibited because of the strong spatial dependence of the electric field so that $\delta_Q E_m^i \neq \delta_Q E_m^j$ for a given quantum number m. Since the effect of distinct quadrupolar shifts of states with *distinct* m values has been examined in (i) above, we replace Eq. (42) by $|\delta_Q E_m^i - \delta_Q E_m^j| < \hbar\gamma m B_L$, which states that, *for a fixed* m, the difference in quadrupolar shifts of neighboring nuclei is smaller than the Zeeman energy in the local field. The latter condition allows us to estimate the characteristic radius r_Q of the zone outside which a spin temperature exists, using the following value of $\delta_Q E_m^i$, obtained by second-order perturbation,

$$\delta_Q E_m^i = \hbar\gamma b_Q \bar{E}(r_i)\frac{2mb_Q\bar{E}(r_i)}{B}\left\{\frac{\bar{E}_\perp^2(r_i,\theta)}{\bar{E}^2(r_i)}[4I(I+1)-8m^2-1]-\frac{\bar{E}_\parallel^2(r_i,\theta)}{\bar{E}^2(r_i)}[2I(I+1)-2m^2-1]\right\}, \qquad (43)$$

where $\bar{E}(r_i)=[1-s(r)\Gamma_t]E_{\mathrm{off}}(r_i)$ is the time average of the electric field. Due to the presence of the magnetic field B at the denominator of the latter equation, the radius r_Q decreases with increasing magnetic field. Derivating Eq. (43) with respect to distance, we find for r_Q an expression of the type

$$r_Q = \eta B^{-1/5}. \qquad (44)$$

The radius r_Q is largest when the electric field is parallel to z, when $\Gamma_t \ll 1$ so that $\bar{E}(r_i) \approx E_{\mathrm{off}}(r_i)$ and for $m=3/2$ in the case of $I=3/2$. In the latter case, taking into account of the fact that in GaAs the *i-j* direction is along the [110] crystal axis, and using the known interatomic spacing, we find $\eta \approx 3\ \mathrm{nm\ T^{1/5}}$. It is concluded that, at a distance r from the donor, the hypothesis of nuclear-spin temperature is valid provided

$$B > B_Q' = \left(\frac{\eta}{r}\right)^5. \qquad (45)$$

Since most of the effects discussed above occur for distances larger than $r = a_0^*/2$, B_Q' is evaluated to ~ 0.09 T. Although much larger than B_L and B_Q defined by Eq. (41), the latter value is smaller than magnetic fields used in most experiments.

For smaller magnetic fields, the evolution of the mean nuclear-spin value $\langle\vec{I}\rangle$, calculated using Eq. (12) and $\langle\vec{I}\rangle = \mathrm{Tr}(\sigma\vec{I})$, is found to be nonexponential as a function of time so that the calculation of the steady-state nuclear magnetization becomes intricate. However, qualitatively, the decrease of the steady-state nuclear magnetization is still expressed by an equation of the same type as Eq. (25) with distinct numerical factors, so that the magnetization is still strongly reduced. Furthermore, because of the very weak magnetic-field dependence of r_Q, the conclusions of the present work are still qualitatively correct for $B < B_Q'$: For a magnetic field equal to $B_Q'/3$, one has $r_Q \approx 0.6a_0^*$. As seen using Eq. (37), such increase is of moderate impact on the nuclear field value since the relative increase of the nuclear field when r_Q increases between $0.5a_0^*$ and $0.6a_0^*$, of 50%, is much smaller than the decreases found in the present work, of more than 1 order of magnitude.[45]

E. Nuclear field dependence on light excitation power and doping

Here we summarize the results of Secs. III A, III B, and III D and obtain the value of the nuclear field B_n using Eq. (37) and further considering the various processes on which depends B_n. The shallow acceptor concentration N_A is assumed to be larger than the donor one so that the donor levels are unpopulated in the absence of light excitation. As shown in Appendix D, the donor occupancy factor Γ_t, on which depends the quadrupolar radius ρ_Q, is related to the excitation power density P by

$$P = \frac{P_0}{(1-\xi)^2}\left[\Gamma_t + \xi\frac{N_A}{N_D}\right], \qquad (46)$$

where

$$P_0 = Lh\nu k N_A N_D, \qquad (47)$$

$$\xi = \frac{k}{\sigma_c v}\frac{\Gamma_t}{1-\Gamma_t}. \qquad (48)$$

Here $h\nu$ is the photon energy (assumed to be above band gap) and L is the electron diffusion length. The quantity k is the coefficient for bimolecular electron-hole recombination.

Shown in Fig. 3 is the specific case of As^{75} in GaAs, using for illustration purposes $N_D = 10^{22}\ \mathrm{m^{-3}}$, $N_A = 5\times 10^{22}\ \mathrm{m^{-3}}$, $L \sim 5\ \mu\mathrm{m}$,[46] $k \approx 1\times 10^{-14}\ \mathrm{m^3/s}$,[47] and $k/\sigma_c v \approx 10^{-1}$, which corresponds to $T \sim 40$ K.[41] Shown in curve a is the dependence of Γ_t as a function of light excitation power, obtained using Eq. (46). The light excitation power range $P < 0.2P_0$ corresponds to $\Gamma_t < 0.15$ and is not considered here because, as discussed in Sec. III C, spin diffusion becomes dominant. Shown in curve b of Fig. 3 is the power dependence of the quantity $s(\rho_Q)$, obtained using Eqs. (3) and (34)–(36). Immediately, apparent is the fact that, in a relatively broad power range near P_0, corresponding to $\Gamma_t = 0.5$, the nuclear field is decreased with respect to the maximum value of 0.5 imposed by spin diffusion by a factor of about 20. Note that, at high power, the light-induced quadrupolar relaxation still decreases the nuclear field because, as seen from Eqs. (46) and (47), Γ_t, equal to $(1+k/\sigma_c v)^{-1}$, is smaller than unity. In the present case, one finds $P_0 = 2.4\times 10^6\ \mathrm{W/m^2}$, a realistic value.

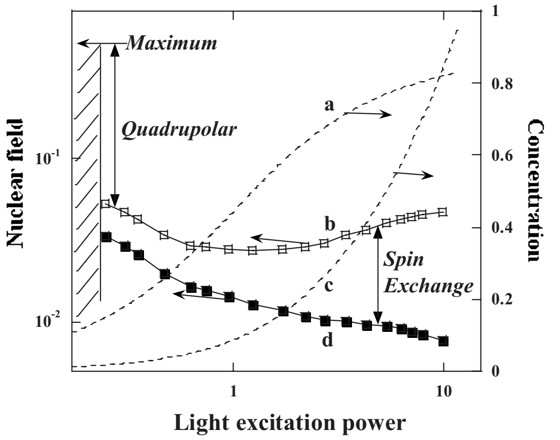

FIG. 3. For As^{75} in GaAs, dependence of the nuclear field on light excitation. The latter quantity is expressed in units of P_0 given by Eq. (47), which depends on doping. The donor and acceptor concentrations are taken as 10^{22} and 5×10^{22} m^{-3}, respectively. Curve a shows the rate Γ_t of donor occupation. Curve b shows the variation of the quantity $s(\rho_Q)$ which expresses the quadrupolar-induced decrease of the nuclear field with respect to its maximum value, estimated using Ref. 28, set by the presence of spin diffusion. Curve c shows the free-electron concentration in units of N_A. Curve d shows the dependence of the reduced nuclear field α_n, given by Eq. (50), which further takes into account the decrease caused by spin exchange between free and trapped electrons. The hatched area marks the zone where the present model is not valid because of spin diffusion (see Sec. III C).

The effective nuclear field, measured experimentally from its effect on the electronic polarization, is further modified by the efficient spin-exchange processes between free and trapped electrons considered in Sec. III A and is equal to the average of the nuclear fields experienced by the two electronic species. Such effect does not modify the quadrupolar radius, but only the multiplicative factor B_{n0} defined by Eq. (37). Assuming, as performed throughout the present work, that the bulk nuclei are weakly polarized, the nuclear field experienced by free electrons is very small so that B_{n0} is proportional to $\Gamma_t N_D/(n_f+\Gamma_t N_D)$ where the concentration of free electrons is given by Eq. (D6). One has finally

$$B_n = \alpha_n b_{n0}\langle S_0\rangle, \tag{49}$$

where b_{n0} does not depend on light power and doping. Since the common mean spin $\langle S_0\rangle$ of free and trapped electrons can be measured from the luminescence polarization, the quantity α_n, given by

$$\alpha_n = \frac{\Gamma_t N_D}{n_f+\Gamma_t N_D}s(\rho_Q) \tag{50}$$

is the reduced nuclear field for which we now consider the power dependence.

Shown in curve c of Fig. 3 is the light excitation dependence of n_f/N_A, obtained using Eq. (D6) and assuming $N_D = N_A/5$. Shown in curve d is the light excitation dependence of α_n. For $P<P_0$, the dominant mechanism for nuclear field reduction is the light-induced quadrupolar relaxation. The nuclear field reduction due to spin exchange becomes significant for $P>P_0$ since n_f increases while Γ_t is nearly constant and induces an overall decrease of the nuclear field with light excitation power.[48]

The effect of a change of *doping* of the quadrupolar-induced reduction of nuclear field is limited to the sole variation of the quantity P_0. As a result, an increase of acceptor and donor doping levels simply shifts curve b of Fig. 3 along the X axis by a similar factor without any change of shape. As seen from Eq. (50), this is still true if one includes the effect of spin exchange, provided the ratio N_A/N_D remains constant. Note finally that *resonant excitation* of donor states might enable to increase the nuclear field value: As seen from Eqs. (23), (32), and (50), the subsequent decrease of the free-electron concentration should induce an increase of the efficiency of the hyperfine relaxation and a decrease of the effect of spin exchange.

We now discuss the possibility of experimental demonstration of the light-induced quadrupolar relaxation. In order to separate the contribution to the nuclear field value of the light-induced quadrupolar relaxation from that of spin exchange with free electrons, it is crucial to analyze the dependence of the nuclear field as a function of light excitation and donor concentration. However, among the experimental works which have estimated the leakage factor f,[22,23,29] none of them has performed the latter analysis, so that experimental proof of the present mechanism is lacking. Such analysis is beyond the scope of the present paper and will be published elsewhere for the case of quantum dots.[37]

IV. CONCLUSION

We now summarize the main results of the present work.

(a) The effect of the light-induced quadrupolar relaxation is evaluated assuming that there exists a temperature among the nuclear-spin system. The latter hypothesis implies that the external magnetic field is sufficiently large to decrease the difference between the quadrupolar shifts of neighboring nuclei so that flip-flops are allowed. In the latter case, the time evolution of the nuclear-spin temperature is found to be exponential, so that a relaxation time can be defined. The latter time T_{1Q}, within numerical factors, depends on the product of the square of the modulation amplitude and of the correlation time of the modulation. Comparison of T_{1Q} with the relaxation time due to the hyperfine contact interaction gives the expression for the nuclear polarization as a function of the distance to the donor under the combined effects of quadrupolar and hyperfine relaxations.

(b) Near shallow donors in semiconductors, the angular-averaged effect of the quadrupolar relaxation is to replace the diffusion radius ρ_D up to which the nuclei are spin-polarized by a smaller, radius called the *quadrupolar radius* ρ_Q.

(c) The quadrupolar-induced decrease of the nuclear field occurs in conditions of light excitation corresponding to partial donor occupancy by photoelectrons. This should induce a decrease of the nuclear field by more than 1 order of magnitude in GaAs and by slightly smaller factors for InP and GaSb. In addition, the effect of averaging of the nuclear field between free and trapped electrons, due to spin exchange, produces a further decrease of the nuclear field for larger light excitation powers.

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APPENDIX A: FORM AND MAGNITUDE OF THE QUADRUPOLAR HAMILTONIAN

We consider here the general case, described by Fig. 4, where both the electric-field direction Z and the magnetic-field one Z' do not coincide with a crystal axis z, taken perpendicular to the crystal surface. The quadrupolar Hamiltonian H_Q of a given nucleus at position $\vec{r}$ is related to the components of the electric-field gradient by[38,39]

$$\begin{aligned}H_Q(\vec{r}) = \frac{eQ}{4I(2I-1)}\Big\{ & V_{Z'Z'}(\vec{r})[3I_{Z'}^2 - I(I+1)] \\ & + V_{X'Z'}(\vec{r})[I_{Z'}(I_{+'}+I_{-'}) + (I_{+'}+I_{-'})I_{Z'}] - iV_{Y'Z'}(\vec{r}) \\ & \times[I_{Z'}(I_{+'}-I_{-'}) + (I_{+'}-I_{-'})I_{Z'}] + \frac{1}{2}[V_{X'X'}(\vec{r}) \\ & - V_{Y'Y'}(\vec{r})][I_{+'}^2 + I_{-'}^2] - iV_{X'Y'}(\vec{r})[I_{+'}^2 - I_{-'}^2]\Big\}, \end{aligned} \tag{A1}$$

where the quantization axis Z' is the magnetic-field direction, the spin operators $I_{\pm'}$ are equal to $I_{X'} \pm iI_{Y'}$, and

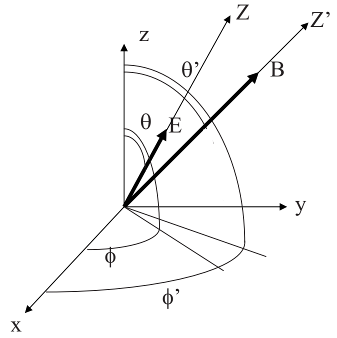

FIG. 4. Geometry of the magnetic-field and electric-field configurations. For clarity, the X (X') axis, which lie in the zZ ($z'Z'$) plane, and the Y (Y') axis, which lie perpendicular to this plane, have been omitted.

$$V_{ij}(\vec{r}) = \frac{\partial^2 E(\vec{r})}{\partial X_i' \, \partial X_j'}, \tag{A2}$$

and X_i' stands for X', Y', or Z'. These directions are distinct from the xyz directions of the cubic crystal lattice, z being also the normal to the sample surface. The components of the electric-field-gradient tensor in the $X'Y'Z'$ frame are obtained by using elementary rules for tensor transformation and are given by[35]

$$\begin{pmatrix} V_{X'X'} \\ V_{Y'Y'} \\ V_{Z'Z'} \\ V_{Y'Z'} \\ V_{X'Z'} \\ V_{X'Y'} \end{pmatrix} = R_{14} \begin{pmatrix} -\sin 2\theta' \sin\varphi' & -\sin 2\theta' \cos\varphi' & \cos^2\theta' \sin 2\varphi' \\ 0 & 0 & -\sin 2\varphi' \\ \sin 2\theta' \sin\varphi' & \sin 2\theta' \cos\varphi' & \sin^2\theta' \sin 2\varphi' \\ \cos\theta' \cos\varphi' & -\cos\theta' \sin\varphi' & \sin\theta' \cos 2\varphi' \\ \cos 2\theta' \sin\varphi' & \cos 2\theta' \cos\varphi' & \frac{1}{2}\sin 2\theta' \sin 2\varphi' \\ -\sin\theta' \cos\phi' & \sin\theta' \sin\varphi' & \cos\theta' \cos 2\varphi' \end{pmatrix} \begin{pmatrix} E_x \\ E_y \\ E_z \end{pmatrix}, \tag{A3}$$

where, as shown in Fig. 4, θ and φ are the angles between Z and z and between x and the zZ plane, respectively, and θ' and φ' are the angles between z and Z' and between x and the zZ' plane, respectively. Here, R_{14} is the sum of an ionic contribution (which depends on the ionicity of the solid, on ε^2-n, where n is the infrared optical index, and on the antishielding factor) and of the covalent contribution (which further depends on the band-gap value).[33]

The expression of the quadrupolar Hamiltonian is then obtained from Eqs. (A1) and (A3). For an arbitrary orientation of the magnetic field, this expression is intricate and depends both on θ' and φ'. If the magnetic-field B direction coincides with a [100] crystal axis $z(\theta'=\varphi'=0)$, the only nonzero components of V_{ij} in the xyz frame are

$$V_{xy} = R_{14}E(\vec{r})\cos\theta,$$

$$V_{yz} = R_{14}E(\vec{r})\sin\theta\cos\varphi,$$

$$V_{zx} = R_{14}E(\vec{r})\sin\theta\sin\varphi. \tag{A4}$$

Equation (4) is readily obtained.

In order to estimate b_Q, it is necessary to determine R_{14}. One of the first determinations was performed for GaAs, where the effect of application of an electric field along the [111] direction on the quadrupolar splitting of the NMR line was studied.[33] Here, we take the more recent measurements of Ref. 36, which give slightly larger values, arguing that the smaller values obtained in Ref. 33 were due to sample inhomogeneities. For GaAs, InAs, and GaSb, independent estimates of R_{14} were obtained using the broadening of the nuclear acoustic resonance.[34] For GaAs, they differ from the latter value by about a factor of 3–4. As a result, for a nucleus α of InAs or GaSb, we have chosen to determine R_{14}^{α} according to the following scaling involving Refs. 36 and 34:

$$R_{14}^{\alpha} = R_{14}^{\alpha}(\text{Ref. } 34) \cdot \frac{R_{14}^{\text{As}}(\text{Ref. } 36)}{R_{14}^{\text{As}}(\text{Ref. } 34)}. \tag{A5}$$

For In^{115} in InP no estimate of R_{14} has to our knowledge been published. However, R_{14} of In^{115} in InP should not differ from that of In^{115} in InAs by more than a factor of 50% since the ionicities of InAs and InP are identical and since the effect of band gap should be similar to the ratio of the R_{14} values of As^{75} between GaAs and InAs. The final results are shown in Table I.

APPENDIX B: CORRELATION FUNCTIONS OF THE QUADRUPOLAR AND HYPERFINE INTERACTIONS

The modulation of the quadrupolar interaction is described by the function $h(t)$, given by Eq. (8). This function is of zero average and takes two discrete values h_{α} (where $\alpha=1,2$) given, respectively, by $h_1 = s\Gamma_t(1-s\Gamma_t)^{-1}$ and $h_2 = -s(1-\Gamma_t)(1-s\Gamma_t)^{-1}$, with respective probabilities $w_1=\Gamma_t$ and $w_2 = 1-\Gamma_t$. The correlation function is written under the form

$$g_Q(\tau) = \langle h(t)h(t-\tau)\rangle = \sum_{\alpha} h_{\alpha} w_{\alpha} \sum_{\beta} h_{\beta} P_{\alpha\beta}(\tau), \tag{B1}$$

where $P_{\alpha\beta}(\tau)$ is the conditional probability that $h=h_{\beta}$ at time τ under the condition that $h=h_{\alpha}$ at time $t=0$.

Assuming that the fluctuation process is Markovian and stationary, the quantity $P_{\alpha\beta}(\tau)$ is given by[49]

$$\frac{dP_{\alpha\beta}}{dt} = \sum_{\gamma} \Pi(\gamma,\beta) P_{\alpha\beta}(t), \tag{B2}$$

where $\Pi(\gamma,\beta)$ is a numerical factor, equal for $\gamma \neq \beta$ to the probability per unit time that $h(t)$ goes from the value h_{γ} to the value h_{β}. The quantity $\Pi(\beta,\beta)$ is the probability that $h(t)$ goes from f_{β} to the other value. One has $\Pi(1,2)=\tau_1^{-1}$, $\Pi(2,1)=\tau_2^{-1}$, $\Pi(2,2)=-\tau_1^{-1}$, $\Pi(1,1)=-\tau_2^{-1}$, where τ_{α} is the lifetime of state α. (With the definitions of Sec. II A, one has $\tau_1=\tau_r$ and $\tau_2=\tau_c$.) Using the latter values, resolution of Eq. (B2) yields

$$P_{11} = (1-\Gamma_t) + \Gamma_t \exp[-t(\tau_1^{-1}+\tau_2^{-1})],$$

$$P_{21} = (1-\Gamma_t) - (1-\Gamma_t)\exp[-t(\tau_1^{-1}+\tau_2^{-1})],$$

$$P_{12} = \Gamma_t - \Gamma_t \exp[-t(\tau_1^{-1}+\tau_2^{-1})],$$

$$P_{22} = \Gamma_t + (1-\Gamma_t)\exp[-t(\tau_1^{-1}+\tau_2^{-1})]. \tag{B3}$$

The result of Eq. (10) is obtained after replacing $P_{\alpha\beta}$ by their latter values in Eq. (B1).

The same procedure can be applied to calculate the correlation function for the hyperfine interaction. Here three states, labeled +1, −1, or 0 are considered, depending on the absence or presence of an electron of a spin equal to +1/2 or −1/2. In addition with the recombination time τ_r, the correlation time also depends on the spin-lattice relaxation time T_1 and of the characteristic time τ_{ex} due to possible spin-exchange processes with delocalized electrons. The final expression for the correlation function, valid in the limit of small electronic polarizations (i.e. $\tau_{\text{ex}}^{-1}+T_1^{-1} \gg \tau_r^{-1}$), is

$$g_H(\tau) = \Gamma_t e^{-|\tau|/\tau_{cH}}, \tag{B4}$$

where τ_{cH} is given by Eq. (32). Equation (B4) expresses the fact that, unlike for the quadrupolar coupling, the hyperfine relaxation is inefficient in the only case where the probability Γ_t of occupation of the localized state is zero.

APPENDIX C: EXPRESSION OF $K_k(\theta)$ DEFINED BY EQ. (16)

Applying the relations $\text{Tr}(ABC)=\text{Tr}(BCA)$ and $\text{Tr}\{A[B,[C,D]]\}=\text{Tr}\{[A,B][C,D]\}$, where A, B, C, and D are spin operators, one obtains

$$\text{Tr}\{I_z[A_{Q,k},[A_{Q,k}^{+},I_z]]\} = \text{Tr}\{[I_z,A_{Q,k}][A_{Q,k}^{+},I_z]\}. \tag{C1}$$

One finds

$$\text{Tr}\{I_z[A_{Q,2},[A_{Q,2}^{+},I_z]]\} = \sin^2\theta \frac{\text{Tr}[(I_+I_-)^2+2I_-I_+I_z]}{\text{Tr}[I_z^2]}, \tag{C2}$$

$$\text{Tr}\{I_z[A_{Q,3},[A_{Q,3}^{+},I_z]]\} = 4\cos^2\theta \frac{\text{Tr}[(I_+I_-)^2+2I_-I_+I_z]}{\text{Tr}[I_z^2]}. \tag{C3}$$

The calculation proceeds using the following relations, where m is the quantum number of I_z,

$$I_{\pm}I_{\mp}|m\rangle = [I(I+1)-m(m\mp 1)]|m\rangle, \tag{C4}$$

$$\text{Tr}(I_z^2) = \frac{1}{3}I(I+1)(2I+1), \tag{C5}$$

$$\text{Tr}(I_z^4) = \frac{1}{5}I(I+1)(2I+1)\left[I(I+1)-\frac{1}{3}\right], \tag{C6}$$

and gives the results shown in Eqs. (17) and (18).

APPENDIX D: CALCULATION OF THE RATE Γ_t OF DONOR OCCUPATION

Complete calculation of Γ_t requires considering the kinetics of generation and recombination for the conduction band, the valence band, and the donor and acceptor levels. Although tractable, such calculation leads to intricate results. We assume here, for simplicity and for illustration purposes, that the kinetics of generation and recombination of acceptor levels and of valence holes are similar. Such assumption is reasonable because donor-acceptor recombination, which is specific to holes trapped at shallow acceptors, is known to be less efficient than band to band or exciton recombination.[50] As a result, we consider only one hole specie, for which the total concentration p is the sum of those of valence holes and of neutral acceptors. In steady state, the rate equations for the concentrations n_f of free electrons and $\Gamma_t\ N_D$ of electrons trapped at donors are, respectively,

$$0 = g - \sigma_c v(1-\Gamma_t)N_D n_f - \frac{n_f}{\tau_r}, \tag{D1}$$

$$0 = \sigma_c v(1-\Gamma_t)N_D n_f - \frac{\Gamma_t N_D}{\tau_r}. \tag{D2}$$

Equation (33) is readily obtained using Eq. (D2). The recombination time τ_r of free and trapped electrons is given by

$$\frac{1}{\tau_r} = kp, \tag{D3}$$

where k describes the bimolecular electron-hole recombination. Writing further that the total concentrations of photo-created holes and electrons are equal, one obtains successively

$$n_f + \Gamma_t N_D = p - N_A, \tag{D4}$$

$$g = n_f\{[\sigma_c v(1-\Gamma_t) + k\Gamma_t]N_D + k[n_f + N_A]\}, \tag{D5}$$

$$n_f = (\Gamma_t N_D + N_A)\frac{k\Gamma_t}{\sigma_c v(1-\Gamma_t) - k\Gamma_t}. \tag{D6}$$

The excitation power density P corresponding to a given value of g is given by

$$P = gLh\nu, \tag{D7}$$

where L is the electron diffusion length and $h\nu$ is the photon energy. The latter equation assumes that the diffusion length is larger than the optical absorption length and that the surface recombination velocity is negligible. Equation (46) is readily obtained using Eqs. (D5)–(D7) and assuming that $N_D \ll N_A$.

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