Nuclear Magnetic Resonance Inverse Spectra of InGaAs Quantum Dots: Atomistic Level Structural Information

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A wealth of atomistic information is buried within a self-assembled quantum dot (QD), carrying the legacy of its chemical composition and the growth history. In the presence of quadrupolar nuclei, as in InGaAs QDs, much of this is inherited to nuclear spins via the coupling between the strain within the polar lattice and the electric quadrupole moments of the nuclei. With this computational study, we aim to identify what sorts of atomistic information can be tapped from a single InGaAs QD, as probed optically by the recently introduced highly sensitive inverse spectra nuclear magnetic resonance technique. To capture the fingerprints of alloying in the spectra, we compare In\(_{1-x}\)Ga\(_x\)As QD with the compound InAs QD of the same shape, as well as performing a search over the parameter space of the inverse spectra technique. We display how both the elemental nuclear properties and local bonding take roles. Among the three elements, the arsenic nuclei with their small gyromagnetic ratio are the most vulnerable to strain at a given magnetic field. Furthermore, because of their large \(S_4\) gradient elastic tensor components, the deviation of the major electric field gradient axis from the static magnetic field is also the largest. Moreover, this axial tilting has a big variance caused by the availability of various arsenic-centric nearest-neighbor configurations under cation alloying. We identify that a signature of alloying as opposed to segregated binaries within the QD is a peak that appears like an additional satellite transition of \(^75\)As. The local chemical and strain environment distinctly affect the isotopic line profiles: while the central transition of the gallium isotopes have a narrow linewidth, those of arsenic and indium are much broader and oppositely skewed with respect to each other. These have nontrivial underpinnings for which we provide an indepth analysis. As the aftermath of random alloying and quadrupole interaction, the nuclei are hosted in a magnetic environment having large local variations. This inhibits the nuclear spin diffusion and gives rise to long nuclear coherence times. We demonstrate the possibility of restoring to a large extend a monoenergetic distribution of isotopic nuclear spins by simply tilting the sample within a range of angles with respect to static magnetic field.

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I. INTRODUCTION

The study of nuclear spins in quantum dots (QDs) over the past decade has revolutionized the traditional research on semiconductor physics.\(^1\)\(^-\)\(^2\) As an essential milestone for the emergent quantum information technologies, the envisioned solid-state quantum memory devices, the envisioned solid-state quantum memories rely on the long coherence times of nuclear spins, with the ultimate aim of bilateral transfer of quantum state between photons and nuclear spins via excitons (see Refs.\(^1\)\(^-\)\(^2\) for reviews of the progress so far). In addition to storing the quantum state, nuclear spins potentially can act as the central processing unit as well as storing the quantum state, nuclear spins potentially can act as the central processing unit as well as in addition to storing the quantum state, nuclear spins potentially can act as the central processing unit as well as in addition to storing the quantum state, nuclear spins potentially can act as the central processing unit as well as in addition to storing the quantum state, nuclear spins potentially can act as the central processing unit as well as in addition to storing the quantum state, nuclear spins potentially can act as the central processing unit as well as in addition to storing the quantum state, nuclear spins potentially can act as the central processing unit as well as in addition to storing the quantum state, nuclear spins potentially can act as the central processing unit as well as in addition to storing the quantum state, nuclear spins potentially can act as the central processing unit as well as in addition to storing the quantum state, nuclear spins potentially can act as the central processing unit as well as in addition to storing the quantum state, nuclear spins potentially can act as the central processing unit as well.
neous and anisotropic strain. In a III-V crystal lattice, such a strain field causes local electric field gradients (EFG) with which a quadrupolar spin-$I$ nucleus, i.e., with $I \geq 1$, interacts because of its electric quadrupole moment. This quadrupole interaction (QI) splits the nuclear spin degeneracy even in the absence of an external magnetic field, and severely broadens the resonances. This has posed a challenge for employing standard ODNMR in SAQDs giving rise to poor signal to noise ratio. Very recently the problem has been alleviated by introducing a so-called inverted rf excitation scheme, thereby increasing substantially the fraction of nuclei participating in the Overhauser shift. This advancement is a breakthrough not only for the atomistic level structural information on strained SAQDs, but also for the quantum information technologies, as it provides crucial structural information needed to engineer noise-free nuclear spin bath and also to perform a coherent control over the Bloch sphere of relatively small number of nuclear spins.

After this successful experimental demonstration of the ODNMR inverse spectra on strained QDs, its full potentials need to be explored on a theoretical level. Therefore, the aim of this work is to undertake a computational assessment, choosing InGaAs QDs as the test case. Primarily, we would like to address what kind of atomistic level information can possibly be extracted by the technique, and where to look for these. In particular we give special importance to the central transition line-shape as this is experimentally the most resolved spectral feature and it carries important clues about the internal structure of the QD. To meet these goals, we perform a detailed search over the parameter space of the inverse spectra technique, in relation to line profiles and resolution trade offs, as well as experimentally more impracticable aspects such as the dependence of the sample orientation with respect to the magnetic field. By comparing a binary InAs QD with an identical-shape alloy In$_{1.2}$Ga$_{0.8}$As counterpart, we uncover key fingerprints of the alloy composition, and describe the basis of these behaviors in terms of available atomistic configurations. Our findings manifest that the inverse spectra technique has the means and the sensitivity to resolve atomistic level variations in a strained nanostructure.

The paper is organized as follows: in Sec. II we present the theoretical setting of our atomistic analysis; in Sec. III we provide information about our test cases, followed by our results grouped into general spectral aspects, line profiles, atomistic origin of quadrupole axial tilting, and the effects of sample tilting with respect to magnetic field; in Sec. IV we summarize our conclusions. There are two appendix sections: the first one discusses nuclear polarizations, and more specifically why it is harder to polarize the arsenic nuclei in a strained environment; the second one illustrates the effects of various EFG parameter combinations on spectral transitions of a single-nucleus as demonstrated on $^{115}$In.

II. THEORY

A. Three Concomitant Coordinate Systems

The crux of our analysis is based on the simultaneous use of a number of coordinate systems. A QD has a native coordinate system set through the crystallographic axes where the QD growth axis usually coincides with one of them; in our test cases this is the $z$-axis and the [001] direction. The orientations of an external magnetic field and the optical beam with respect to the growth axis of the QD bear particular significance in terms of which Faraday/Voigt geometries and $\sigma^k$ pumping are defined. Yet, there are at least two more relevant coordinate axes that gain importance in an atomistic treatment. Unlike the global crystal axes, these are local, i.e., changing orientation with position over the QD. They are defined through strain and the EFG tensors, denoted in cubic crystallographic $xyz$ components by $\epsilon_{ij}$ and $V_{ij}$, respectively. The two phenomena are linked through $S$, the fourth-rank gradient elastic tensor as

$$V_{ij} \equiv \frac{\partial^2 V}{\partial x_i \partial x_j} = \sum_{k,l=1}^{3} S_{ijkl} \epsilon_{kl},$$

where $V$ is the crystal potential. In the so-called Voigt notation, $S$ tensor for cubic crystals is governed by only two independent components $S_{11}$ and $S_{44}$, both of which are experimentally measurable. In cubic crystallographic $xyz$ axes, $S_{11}$ and $S_{44}$ relate the diagonal and off-diagonal strain and EFG components, respectively, like $V_{zz} = S_{11} \epsilon_B$, $V_{xy} = 2S_{44} \epsilon_{xy}$, etc., where $\epsilon_B = \epsilon_{zz} - (\epsilon_{xx} + \epsilon_{yy})/2$ is the so-called biaxial strain. Similarly, we find it necessary to introduce a shear strain measure as $\epsilon_S = |\epsilon_{xy}| + |\epsilon_{yz}| + |\epsilon_{zx}|$ to quantify the effectiveness of the off-diagonal components.

The strain and EFG tensors have their own distinct principal axes where each becomes diagonal, and within which working with that quantity becomes highly convenient. Among the three principal axes of a rank-2 quantity (such as strain or EFG), the one with the largest absolute value is named as the major principal axis. Hence, this brings three concomitant coordinate systems at one’s disposal. Our primary interest on nuclear spin states in the presence of QI favors the explicit use of local EFG principal axes which we shall discriminate by the XYZ capital letters, with axes being labeled so as to satisfy the inequalities $|V_{XX}| \leq |V_{YY}| \leq |V_{ZZ}|$, making $Z$ the major EFG axis.

B. Fundamental Hamiltonian

In the local $XYZ$ frame the strain-dependent part of the nuclear Hamiltonian responsible for the QI is given
by

$$\mathcal{H}_Q = \frac{e^2 q Q}{4 I (2I-1)} \left[ 3T_Z^2 - T^2 + n \frac{T^2_+ - T^2_-}{2} \right],$$

(2)

where \( \vec{T} \) is the dimensionless nuclear spin angular momentum vector operator, through which we define the above raising/lowering operators \( I_\pm = I_X \pm i I_Y \). As the other variables, \( Q \) is the electric quadrupole moment of the nucleus, \( q \equiv V_{ZZ} / e \) is the EFG parameter, with \( e > 0 \) being the electronic charge, and \( n = (V_{XX} - V_{YY}) / V_{ZZ} \) is the biaxiality parameter. The former is the primary coupling constant of QI, and the latter determines the mixing between the free nuclear spin magnetic quantum numbers.

In the same local XYZ frame the static magnetic field vector \( \vec{B}_0 \) will be in general oblique as governed by the spherical polar angles \( \theta \), and \( \phi \) so that its Hamiltonian becomes

$$\mathcal{H}_M = -\hbar \Omega (I_X \sin \theta \cos \phi + I_Y \sin \theta \sin \phi + I_Z \cos \theta),$$

where \( \Omega \equiv \gamma B_0 \), and \( \gamma \) is the nuclear gyromagnetic ratio. Hence, for each nucleus \( k \) under consideration,

$$\mathcal{H}_Q \equiv \mathcal{H}_M (|i \rangle_k) = \nu^k \langle i \rangle_k,$$

needs to be solved, where we denote the resultant spectrum with \( \nu^k \), \( i = -I, -I + 1, \ldots, I \). Under sufficiently high magnetic fields, which we assume throughout our work, dipole-allowed transitions are \( i \leftrightarrow i + 1 \). Among these, the strongest one \( -1/2 \leftrightarrow +1/2 \) is referred to as the central transition (CT), and the remaining weaker ones as the satellite transitions (STs). When EFG major principal axis deviates from \( \vec{B}_0 \), CT becomes broadened only as a second-order effect, hence stays quite narrow, whereas STs undergo extensive broadening as they are affected in first-order.

\[ \text{C. Optical Orientation} \]

We characterize the nuclear spin ensemble within the QD by a nuclear spin temperature \( T_{\text{nuc}} \) which is a measure of the degree of optical orientation. The probability of occupancy of each nuclear spin state, \( i \) is governed by a thermal distribution of the form

$$p_i^\text{th} = \frac{e^{-\hbar \nu^k_i / k_B T_{\text{nuc}}}}{\sum_{i=-I}^I e^{-\hbar \nu^k_i / k_B T_{\text{nuc}}}},$$

where \( k_B \) is the Boltzmann constant.

The helicity of the absorbed optical orientation beam dictates the spin of the created electron and hole as a requirement of angular momentum conservation. Subsequently, through predominantly the contact hyperfine interaction between the electron and nuclear spins, depending on the absorbed photon helicity the nuclei are either pumped down or up within their individual spectrum \( \nu^k_i \), toward \( i \rightarrow -I \) or \( i \rightarrow +I \), respectively. In the absence of an rf excitation, and under continuous optical orientation this distribution will be sustained. Therefore, the steady-state is either normal for \( \sigma^+ \), or inverted for \( \sigma^- \) persistent pumping. We represent the former (latter) by using a positive (negative) nuclear spin temperature, i.e., \( T_{\text{nuc}} > 0 \) \((T_{\text{nuc}} < 0)\).

\[ \text{D. rf Excitation} \]

The novelty of the inverse spectra technique with respect to conventional saturation spectroscopy comes from its flipped excitation scheme, which has a white spectrum except for an intermission of frequency, \( f_{\text{sat}} \). If this gap does not coincide with any of the dipole-allowed transitions \( \nu^k_i \leftrightarrow \nu^k_{i+1} \), then under a sufficiently long excitation, the population of all nuclear spin states will be equilibrated at a same value, \( p_i^\text{sat} = 1/(2I + 1) \), giving rise to zero nuclear polarization, and hence no Overhauser shift on the excitonic PL. On the other hand when the gap coincides with one, or sometimes simultaneously with a number of transitions, the equilibration will only occur within the states that remain under the gap-free parts of the excitation. Therefore, the \( 2I + 1 \) states will be split into multiple groups each internally reaching to an individual saturation value based on the preexisting thermal populations of the member states according to

$$p_i^\text{sat} = \frac{\sum_{G \in G} \tilde{p}_i^G}{N_G},$$

where \( G \) is the group index, and \( N_G \) is the number of member spin states within that group.

The spin polarization of a nucleus \( k \) just after rf excitation will be based on the population of each state

$$\vec{P}_k = \frac{1}{I} \sum_{i=-I}^I \langle i | \vec{T} | i \rangle_k p_i^\text{sat}.$$

If we denote by \( \hat{\vec{e}} \) the optical pumping direction along which the electronic spin is aligned, which is usually, but not always the QD growth axis, then the parallel component of the nuclear polarization becomes \( P_k^e = \hat{\vec{e}} \cdot \vec{P}_k \). In the experiments, the changes in the nuclear polarization are probed via the Overhauser energy shift in the excitonic PL signal, which is given by

$$E_{\text{OS}} = \sum_k |\psi(\vec{R}_k)|^2 A_k I_k P_k^e,$$

where \( A_k \) is the hyperfine coupling constant, and \( \psi(\vec{R}_k) \) is the electronic wave function at the nuclear site. Here, we ignore the hole hyperfine interaction which is about an order of magnitude weaker.
III. RESULTS

A. Test QDs

The detailed chemical composition profile, i.e., local stoichiometry of InGaAs QDs is still an active and unresolved topic. A critical factor that non-trivially affects the uniformity of the indium distribution within the QD is the annealing process. It has been reported that the annealed QDs become less uniform along the lateral, but more uniform along the growth direction; furthermore, the dots get 25% bigger with respect to their pre-annealed sizes in both lateral and growth directions as the indium atoms diffuse inward. We base our comparative analysis on two test cases of lens-shaped QDs having a base diameter of 40 nm and a height of 6 nm. Both QDs have an InAs wetting layer and are embedded into a GaAs host matrix, but differ in their interior compositions, with one QD being InAs, whereas the other being the alloy In$_{0.2}$Ga$_{0.8}$As (see, inset of Fig. 1), where indium and gallium atoms are randomly distributed all over the QD region according to the given mole fraction. Admittedly, these constitute the two extremes, and intermediate cases like partially segregated alloy realizations are not addressed in this work. The uniform alloy composition considered here is expected under high growth rate conditions, where the landing atoms on the surface do not have time to segregate into binary compounds, as they quickly get covered by the next layer. The rationale behind the selection of these two cases is based on their distinct strain, and hence quadrupolar characteristics.

The computational supercell contains more than 2 million atoms, most of them residing in the host matrix, and the QD itself has 171,884 atoms. We follow the procedure presented in Ref. 20 for the relaxation of the embedded QDs to their final structures, and the extraction of the atomistic strain distributions. The only exception in the present work is that we do not perform any nearest-neighbor strain averaging as this would hinder the true linewidths of the isotope-dependent NMR spectra.

B. General spectral aspects

The inverse spectra for both QDs are shown in Fig. 1. For a spin-$3/2$ nucleus $^{115}$In, $T_{1\text{nuc}} = 5 \text{ mK}$, $\sigma^+$ optical pumping. Inset shows corresponding QD atoms over the (100) cross section.

The contribution of individual isotopic species as well as the dependence on the light helicity with respect to external magnetic field are displayed in Fig. 2. Even though the number of arsenic nuclei is the largest, their CT resonance has the smallest peak, the reason of which is related to the hardness in polarizing the arsenic nuclei as elaborated further in Appendix A. The indium nuclei because of their 9/2 spins, have much extended STs as can be observed from the upper panel of Fig. 2. The magnitude orderings of the neighboring STs on either side of the CT are seen to be switched by changing pumping helicity (see, Fig. 2 lower panel), as a matter of fact the contrast can become even larger, as is the case in the original experiment. Also note that to enhance the small differences, here we prefer to use a larger $f_{\text{exp}}$ value of 800 kHz.

In experiments, the choice of $f_{\text{exp}}$ value can indeed become a crucial decision for the inverse spectra. To highlight the trade off between spectral resolution and the signal intensity, in Fig. 3 we display the spectral evolution as a function of $f_{\text{exp}}$ for each isotopic species. The resolution-limited flat-top profiles quickly emerge for the gallium nuclei indicating their narrow linewidths as will be analyzed below in more depth. On the other hand, for indium and especially arsenic nuclei, a large $f_{\text{exp}}$ value may still be preferred which is particularly beneficial to capture the relatively weak features associated with the STs. One example for this is the emergence under larger $f_{\text{exp}}$ values of an additional ST peak as indicated by an arrow on the top left arsenic panel of Fig. 3. For a spin-$3/2$ system only three peaks are expected, namely, $3/2 \rightarrow 1/2$, $1/2 \rightarrow -1/2$, and $-1/2 \rightarrow 3/2$. Therefore, this fourth peak which unambiguously belong to arsenic nuclei (see, Fig. 2 top panel) is rather curious. We identify it as the alloy peak with a reasoning based on an atomistic configuration analysis, however deferring its detailed discussion for
C. Central transition linewidth and profile

Much about the nuclear spin environment can be learned by simply focusing on the CT lineshape. For this purpose, first we select a small $f_{\text{exp}} = 1 \text{ kHz}$, which is ultimately limited by the nuclear homogeneous linewidth.\textsuperscript{40} Considering alloy In$_{0.2}$Ga$_{0.8}$As QD, CT line profiles at different magnetic fields are shown in Fig. 3. We should note that as there always remains some residual overlap from the ST of the other isotopic species, here the individual isotopic contributions, and not the total signals are plotted. These isotopic line profiles display distinct features, such as $^{69}$Ga and $^{71}$Ga both have quite narrow main peaks over a broad pedestal, while In and As have conspicuously opposite asymmetric lineshapes.

To quantify these trends, we make use of the mean, variance, skewness and kurtosis of these distributions; for a sample $\{x_j\}$ of $N$ data points these quantities are,


\[ \bar{x} = \frac{1}{N} \sum_{j} x_j , \]

\[ \text{Var}(x) = \frac{1}{N-1} \sum_{j} (x_j - \bar{x})^2 , \]

\[ \gamma = \frac{\bar{x} - M}{\sigma} , \]

\[ \text{Kurt}(x) = \left[ \frac{1}{N} \sum_{j} \left( \frac{x_j - \bar{x}}{\sigma} \right)^4 \right] - 3 , \]

where among a number of alternatives we prefer Pearson’s mode skewness measure, \( \gamma \), with \( \sigma = \sqrt{\text{Var}(x)} \) being the standard deviation, and \( M \) is the mode (peak value) of the distribution. Skewness is a dimensionless asymmetry parameter; for unimodal cases zero skewness corresponds to a symmetric distribution around its mode so that tails on either side balance out. Kurtosis is a dimensionless measure of relative peakedness or flatness of a distribution; for a normal distribution zero skewness corresponds to a symmetric distribution.

We employ these shape quantifiers on the CT of alloy In\(_{0.2}\)Ga\(_{0.8}\)As QD for all isotopes as illustrated in Fig. 5 which not only corroborate well with the observations of Fig. 4 but also reveal some additional trends. For all isotopes the standard deviations diverge as the magnetic field decrease below 2 T into the QI-dominant regime. The \( ^{71}\text{Ga} \) isotope has the narrowest \( \sigma \) which is also matched by \( ^{69}\text{Ga} \) at high magnetic fields. Regarding skewness, \( ^{71}\text{Ga} \) monotonically changes its asymmetry from red- to blue-tailed making a transition at 5 T. As was qualitatively noted from Fig. 4, Fig. 5 quantitatively asserts that In and As possess opposite skewness, a point which we shall discuss further after we layout the atomistic structural analysis. Finally, from the kurtosis panel we observe that all isotopes start from a flat distribution within the QI-dominant regime at low magnetic fields which evolves to a peaked shape at higher fields. Gallium isotopes go through maxima around 4 T and 9 T for \( ^{71}\text{Ga} \) and \( ^{69}\text{Ga} \), respectively.

**How do nuclear quadrupole parameters affect the lineshape?** Figure 6 illustrates the way CT profile changes as the nuclear quadrupole parameters \( (Q, S_{44}, S_{11}) \) of As are artificially varied. First of all, if we double the electric quadrupole moment \( Q \), the red-tailed asymmetry is enhanced indicating that its origin is the QI. In particular, the \( S_{44} \) component of the gradient elastic tensor primarily controls the asymmetric profile: as seen from Fig. 6 lowering this value to that of Ga (i.e., decreasing by about 2.5 times) drastically reduces the asymmetry, while setting it to zero totally removes and even reverses its direction. Since \( S_{44} \) relates the off-diagonal entries of EFG and the strain tensors, its effectiveness directly invokes to the importance of shear strain on the CT asymmetry. On the other hand, \( S_{11} \) component is not functional, doubling its value virtually leaves the asymmetry unchanged. Note that all of the above statements refer to the In\(_{0.2}\)Ga\(_{0.8}\)As QD. Additionally, in the bottom panel of Fig. 6 we compare the alloy QD with the binary InAs QD, where in the latter the CT asymmetry of As nuclei gets significantly enhanced. This is at odds with the established insight so far based on the prime importance of the shear strain, in conjunction with its small value for binary InAs QD. As a matter of fact as shown on the left column of Fig. 7 the interior of the In\(_{0.2}\)Ga\(_{0.8}\)As QD retains an exuberant shear strain profile due to ran-
dom alloying, whereas this gets diminished in the core of the InAs QD and only becomes significant toward the interfaces. However, a change of roles is observed on the right column of the same figure where the compound QD has much stronger biaxial strain compared to alloy QD simply due to larger lattice mismatch between the core and the matrix regions. As we shall see in the atomistic analysis to follow and Appendix B, not only shear but also the biaxial strain component can cause a shift in CT; the former acts through EFG axial tilting as in alloy QI, whereas this gets diminished in the core.

D. Alloy bonding and consequences of quadrupole axial tilting

The pronounced spread of quadrupole axial tilting of the As nuclei can be linked to the combined effect of the large variation in the shear strain component, $\epsilon_S$ of As atoms, compounded by the particularly high $S_{44}$ value of As nuclei that is more than 2.5 times of those of Ga and In values. The large variance in $\epsilon_S$ of As has a chemical origin which stems from the mixed cation neighbors in the tetrahedral bonding: center As atom is coordinated with different number of Ga/In atoms depending on the local alloy realization, see Table II for the corresponding tilt angles, $\theta$ of the major EFG axes in each bonding configuration. This is in support of a recent NMR study which concludes that $^{75}$As QI is highly sensitive to different cation coordinations. In the case of In or Ga atoms their nearest neighbors are always As, thus, the local strain variation in the cations (Ga, In) is more of a next-nearest-neighbor effect.

Figures 8 and 9 display for the alloy and compound QDs respectively, the histograms for the three EFG parameters, namely, major quadrupole axial tilting away from the static magnetic field, $\theta$; the value of the major EFG, $V_{ZZ}$; and the EFG biaxiality, $\eta$. Starting with axial tilting for the alloy $\text{In}_{0.2}\text{Ga}_{0.8}\text{As}$ QD (Fig. 8 top row), we observe a remarkable dissimilarity in the histogram of orientations of arsenic nuclei in comparison to cations (Ga,
In). The latter display somewhat similar characteristics, that peaks either along or perpendicular to the magnetic field. As mentioned above, for the cation nuclei (Ga, In) the quadrupole axial tilting is driven by a change in their next nearest neighborhoods. All together there are 144 configurations; we show in Fig. 12 two such gallium-centric instances where a change in the second-nearest neighbor atom switches the major EFG axis from parallel to perpendicular orientation with respect to growth axis. The distribution of the axial tilting of As nuclei has two peaks at 45° and 54.7° that coincide with those pre-relaxed configurations of Table II even obeying the same 1:2 ratio of the relative weights of these cation-bonding orientations. Once again, the role of the rather high $S_{44}$ value of As nuclei is demonstrated by comparing the top left panels of Figs. 8 and 9, where in the latter figure artificially setting $S_{44}$ value to zero sweeps all partially-tilted nuclei toward either 0° or 90°. Next, considering the binary InAs QD (Fig. 9 top center and right panels), due to lack of alloying for this case, both In and As nuclei’s major EFG axes are more or less aligned along the magnetic field. The interface As atoms which are relatively low in number do still have mixed cation neighbors and this gives rise to some limited variance and axial tilting. Analyzing the middle rows in these two histogram figures, in the alloy QD, major EFG values are evenly distributed on either side of zero, and grouped in a few bunches. For the compound QD, the nuclei are gathered around a single $V_{zz}$ value with opposite signs for In and As. The biaxiality parameters $\eta$ (bottom rows) of the two QDs are also markedly different: they are spread over the full accessible range for the alloy QD, whereas the compound QD EFG is quite uniaxial, mainly restricted to lower than the 0.25 value.

**What is the physical implication of large variance in quadrupole axial tilting?** The nuclear dipole-dipole interaction is the main channel for nuclear spin diffusion via pairwise flip-flops. However, if the major quadrupolar alignment of each of the involved nuclei is significantly off, this inhibits a flip-flop event on the basis of energy mismatch. We noted above that the random alloy QD and in particular the As nuclei have a much wider variation in quadrupole axial tilting due to change in local neighborhood as compared to compound QD case. Therefore, QDs with large variance in shear strain are ideal candidates for reduced nuclear spin diffusion, hence prolonged $T_2$ times, as validated by recent experiments (see, Ref. 17, and references therein). In fact, in resemblance to **defect centers** that receive wide attention for spintronics applications, a random alloy In$_{x}$Ga$_{1-x}$As QD especially of low molar fraction can be termed as a **defect colony** with so many indium atoms replacing the gallium of the host lattice.

### E. Hallmark for random alloying in ST band

We now return to the additional ST peak on the top left $^{75}$As panel of Fig. 3 (marked with A and an arrow) which is unexpected for a spin-3/2 system. We attribute this A-peak to the cation-alloying present within the QD. Specifically we trace its origin to the As nuclei with their major quadrupolar EFG axes tilted **perpendicular** to the magnetic field. This can be observed from Fig. 13 where we analyze the contribution of nuclei tagged with respect to their EFG axial tilting. In the case of In nuclei (right panels), we do not see a particularly distinct feature com-
FIG. 10. (Color online) Two-dimensional EFG histograms. Upper two rows: EFG axial tilting, $\theta$ versus the major EFG, $V_{ZZ}$ (in units of $3 \times 10^{21}$ V/m$^2$). Lower two rows: EFG axial tilting, $\theta$ versus the EFG biaxiality, $\eta$. In each group, top rows: In$_{0.2}$Ga$_{0.8}$As QD; lower row left panels: same as top row left panels but with $S_{44}$ value of As nuclei reduced to zero; lower row center and right panels: binary InAs QD. Color code represents the number of nuclei in logarithmic scale.

...ing from the nuclei (very few in number) that are close to perpendicular orientation. In contrast, those for the case of As nuclei within the alloy In$_{0.2}$Ga$_{0.8}$As QD (left top panel) are clearly responsible for the A-peak. Because of the rather different strain environment of these nuclei, a distinct peak occurs (around 39 MHz) markedly separated in frequency from the neighboring ST peak (around 38 MHz). For the InAs QD (bottom left panel), as there is only cation-alloying on the interfaces, there are very few perpendicularly-tilted As nuclei, hence no contribu...
TABLE I. (Color online) Major quadrupole axis orientations, denoted by the angle $\theta$ with respect to the static magnetic field (in these figures, along the vertical direction), for all possible arsenic-centric configurations at their pre-relaxation stages. Note that consecutive local strain relaxation (cf. Fig. 5) will result in a variance around these $\theta$ values.

| # | #1 | #2 | #3 | #4 |
|---|---|---|---|---|
| $\theta$ | $54.7^\circ$ | $54.7^\circ$ | $54.7^\circ$ | $54.7^\circ$ |
| #5 | $54.7^\circ$ | $54.7^\circ$ | $54.7^\circ$ | $54.7^\circ$ |
| #9 | $54.7^\circ$ | $54.7^\circ$ | $54.7^\circ$ | $54.7^\circ$ |
| #13 | $54.7^\circ$ | $54.7^\circ$ | $54.7^\circ$ | $54.7^\circ$ |
| #14 | $89.6^\circ$ | $89.6^\circ$ | $\text{N/A}$ | $\text{N/A}$ |

FIG. 11. (Color online) A schematic illustration for the typical EFG components and orientations for the indium (black/solid arrows) and arsenic (red/dashed arrows) nuclei of alloy In$_x$Ga$_{1-x}$As vs compound InAs QDs.

F. Opposite skewness of As and In CT lineshapes for the random alloy QD

Based on the foregoing atomistic analysis, we can now address the intriguing contrast between the CT lineshape asymmetries of the In and As nuclei as displayed in Figs. 4 and 5. That is, CT profile of In has positive skew (blue-tailed), while that for As has negative skew (red-tailed). The origin of these opposite behaviors is rooted in the corresponding disparity in their EFG characteristcs manifested by two-dimensional histograms in Fig. 10. Specifically, for the case of As, the group of nuclei strongly tilted with $\theta \lesssim 45^\circ$ and $V_{ZZ} \lesssim 0$, and for the case of In those almost untilted $\theta \approx 0^\circ$ but with large $|V_{ZZ}|$ are responsible for the opposite skewness. For the latter, this large $|V_{ZZ}|$ occurs from those In atoms residing in a relatively large biaxial strain environment, unlike the As or Ga atoms in relation to their CT. Making use of the single-nucleus analysis in Appendix B, EFG axial tilt at a constant $|V_{ZZ}|$ causes a red shift of the CT as the tilt increases up to $45^\circ$; on the other hand for the case of nearly untilted nuclei, increasing $|V_{ZZ}|$ and/or increasing EFG biaxiality, $\eta$ both cause a blue shift of the CT. To further support this argument, in Fig. 14 we present major EFG orientation-resolved inverse spectra analysis focusing on the CT. Here, top left panel shows that the red-tailed skewness in As results from the tilted nuclei of angle less than $45^\circ$, while on the top right panel the blue-tailed skewness of In is caused by almost untilted nuclei, $\theta < 3^\circ$. Note that the tilted In nuclei still give rise to red skew but they do not dominate. Indeed, in Fig. 15 we validate that if As (In) nuclei with tilt angle greater than $45^\circ$ ($3^\circ$) are only considered, the red (blue) skewness disappears. Next, returning to the bottom row of Fig. 14 in the case of the binary InAs QD both As and In CT are red skewed, which can also be inferred from their similar 2D EFG histograms in Fig. 11 especially noting the fact that both ensembles have highly uniaxial EFG. Again invoking the single-nucleus insight from Ap-
FIG. 13. (Color online) Contributions to inverse spectra from the nuclei as a function of their major EFG orientations with respect to static magnetic field. Left panels: $^{75}$As nuclei, right panels: $^{115}$In nuclei. (a) Alloy In$_{0.2}$Ga$_{0.8}$As QD, (b) InAs QD. For all cases $B_0 = 5$ T, $f_{gap} = 200$ kHz, and $T_{nuc} = 3$ mK under $\sigma^+$ optical pumping. For the panels on the right, to improve visibility the color scale maxima are set to quarter of their ordinary values.

Appendix B, increase in either the angular tilt or the $|V_{ZZ}|$ both work in the same direction leading to red shift of the CT.

The typical EFG configurations responsible for the In and As CT lineshapes are summarized in Fig. 11. In the alloy QD, strain inflates the EFG biaxiality of both indium and arsenic nuclei; at the same time, in the case of arsenic enhances tilting, and in the case of indium boosts the major EFG. The contrast between these two nuclei disappears in the compound QD. Both have quite uniaxial EFG with some axial tiltings: distribution’s mode for In is $\sim 5^\circ$ and for As it is $\sim 16^\circ$.

G. Satellite transition collapse under sample tilting

To gain somewhat different insight, another two-dimensional spectra can be generated with the added degree of freedom being the tilting of the sample growth axis with respect to the static magnetic field which is also taken to be the direction of optical pump beam. The resultant spectra for binary InAs, and alloy In$_{0.2}$Ga$_{0.8}$As QD are shown in Fig. 14. Here, we observe that around a tilting range of $50^\circ - 54^\circ$, the STs “collapse” on to CT, i.e., rendering all neighboring transitions energetically almost identical. Not surprisingly this is more distinctly the case for the InAs QD. To explain this behavior, in Appendix B we demonstrate on a single $^{115}$In nucleus
how the opposite ST shifts disappear at a tilting angle ranging between $45^\circ$ to $54.5^\circ$ depending on the biaxiality, $\eta$ (cf. Fig. 13). One outcome of this collapse is the reduction of the energy mismatch among the nuclei of the same isotope. Hence, especially for the indium nuclei which have the largest spin-9/2 manifold giving rise to widest spread in energy, one can expect a shorter $T_2$ due to enhanced spin diffusion under the critically tilted angle ($\sim 52^\circ$) with respect to no tilted case.

IV. CONCLUSIONS

This computational study aims to assess the efficacy of the NMR inverse spectra technique as a tool for retrieving atomistic level structural information from strained SAQDs. Through a comparative study of alloy versus compound In(Ga)As QDs, as well as of the involved nuclear species, we unveil marked differences in their spectral features, and establish links with the local chemical structure, strain, and material properties. Our main findings are grouped as follows.

(i) **Strain and CT asymmetry** – In compound QDs dominant component is the biaxial strain which causes quite a uniaxial and rather strong EFG. The shear strain has a secondary role being significant around the interfaces and results in a limited yet crucial EFG axial tilting. Indium and arsenic nuclei qualitatively both obey to this picture. The situation becomes more complex in the alloy QD. As a result of random alloy distribution the shear strain spreads all throughout the core and plays a primary role. Moreover, EFG biaxiality of all elements get enhanced. An interesting aftermath of atomistic alloy strain is that the indium nuclei are mostly untitled but have large EFG values, whereas arsenic nuclei have low EFG values but with exces-
unity to assist the asymmetry comparison. Alloy In with all the nuclei. For each case maxima are normalized to nuclei at 8 T. Painted curves show the original contribution of the static magnetic field, for the As nuclei at 5 T (top), and In nuclei at 8 T. Finally, we predict the collapse of the STs onto CT which is most effective for compound QDs, and the possibility of negating QI and restoring a monoenergetic distribution like a solitary Zeeman interaction, simultaneously for all isotopic nuclear spins by tilting the sample about 52° with respect to static magnetic field.

These findings must be verified experimentally and superseded by further studies for the purposes of both atomistic material insights and also for the coherent control of relatively small number of nuclear spins embedded in a strained confined environment.

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APPENDIX A: NUCLEAR POLARIZATION ALONG THE STATIC MAGNETIC FIELD

In this appendix, we discuss the average nuclear spin orientation for each isotopic ensemble within the alloy In$_{0.2}$Ga$_{0.8}$As QD in the presence of both Zeeman and QI terms. Even though the results here are qualitatively along the normal expectations, the quantitative details and isotopic variations may still be worthwhile considering. In Fig. 17 we show the average nuclear polarization along the static magnetic field, $P$ for each isotopic ensemble as well as the total values, based on the weighted contribution of each isotope within the QD; in part (a), the upper plot depicts nuclear spin temperature dependence at a fixed magnetic field of 5 T, whereas the lower plot shows how it varies with respect to magnetic field at a fixed nuclear spin temperature, $T_{\text{nuc}} = 3$ mK. The latter depends on the optical pumping and nuclear spin energetics. Qualitatively, in both cases all isotopes display the expected polarization trends under increased magnetic field or decreased nuclear spin temperature. More importantly, we observe that there is no apparent roadblock against the full (i.e., 100%) nuclear polarization, albeit requiring rather high magnetic fields and/or low $T_{\text{nuc}}$ values. On the quantitative side, there is a striking difference among the elements, namely arsenic nuclear ensemble’s polarization is substantially lower than the other elements. This is the origin of the mentioned smallest CT peak of arsenic among all elements in Fig. 15. Stated quantitatively, at $B_0 = 5$ T and $T_{\text{nuc}} = 3$ mK, arsenic nuclear spin polarization is about 44%, whereas $^{69}$Ga → 58%, $^{71}$Ga → 68%, and $^{115}$In → 81%. With the largest population belonging to the arsenic nuclei due to alloy partitioning between cations, the overall average polarization value (denoted as total in Fig. 17) comes out as 55%, i.e., closer to that of the arsenic value.

Why is it harder to orient the arsenic nuclei? By far the most critical factor is the gyromagnetic ratio, $\gamma$ which is substantially smaller for arsenic compared to other elements. To illustrate this point, we artificially increase $\gamma$ for $^{75}$As by 55% so that it reaches to the average value.
of the $^{69}$Ga and $^{71}$Ga ensemble. It can be observed in part (b) of Fig. 17 that arsenic as well as the total nuclear polarization now lie in between the $^{69}$Ga and $^{71}$Ga curves. In particular, for $B_0 = 5$ T and $T_{nuc} = 3$ mK, the arsenic spin alignment increases from its actual value of 44% to 62%. The underlying reason is that QI has a bidirectional character; being an electrostatic interaction in nature, it cannot discriminate the states $|\pm m\rangle$, whereas Zeeman interaction being unidirectional splits the $|+m\rangle$ and $|-m\rangle$ states thereby promoting nuclear spin polarization (see, Fig. 18). In other words, while the static magnetic field (Zeeman term) tries to polarize the nuclear spins, QI tries to erase this. Hence, with their low $\gamma$ value, $^{75}$As nuclei are more prone to the quadrupolar depolarization compared to other isotopes at the same external magnetic field. In the case for pure InAs QD (not shown), the trends are similar, however, as this QD is much more strained, here the relevant component is the biaxial strain, $\epsilon_B$, the quadrupolar effects are somewhat more pronounced.

APPENDIX B: SINGLE-NUCLEUS PARTICULAR EFG PARAMETER TRAITS

In this appendix considering a single nucleus governed by the general Hamiltonian, $\mathcal{H}_Q + \mathcal{H}_M$, we present how CT and ST frequencies shift under various combinations of the three EFG parameters: the major EFG value ($V_{ZZ}$), the angular deviation of the major EFG axis from the static magnetic field ($\theta$), and biaxiality ($\eta$). As the trends are qualitatively similar among the nuclear species of this work, for demonstration purposes we choose $^{115}$In. The static magnetic field is taken as 8 T which is used in some of our calculations in the text. Within the STs, we consider the $3/2 \leftrightarrow 1/2$ transition.

Figure 19 displays the variation with respect to each one of $V_{ZZ}$, $\theta$, $\eta$ while keeping the other two parameters fixed. As the shift of CT is in second-order under QI, the dependence on $V_{ZZ}$ is quadratic, hence independent of its sign (top left panel), in contrast, ST shifts being first-order are much stronger (top right panel). For both CT and ST the direction of shift depends on $\theta$. In the case of CT for small angles there is a blue shift with increasing $|V_{ZZ}|$, which becomes a red shift for larger
angles (on top left panel, $10^\circ$ curve). For the specific case considered here ($^{115}\text{In}$ and $\eta = 0.5$) this transition occurs at $\theta = 5.55^\circ$. Yet, for even larger angles this reverts back to a blue shift (e.g., $90^\circ$ curve). The continuous variation of $\theta$ (middle row) produces a cosine-type shift in either CT and ST, again with the effect being much stronger for the latter. Observe that the shifts in ST for $\pm V_{ZZ}$ cross each other at a $\theta$ value ranging between $45^\circ$ and $54.5^\circ$ as $\eta$ varies from 0 to 1. Other STs (for the case of In) display similar pattern. It is this behavior that is harnessed in the collapse of STs at a convenient sample

tilting around $52^\circ$. The bare dependence on $\eta$ can be seen on the bottom row, in particular it shows a blue shift in CT for $\theta = 0$. Rather inhomogeneous mixture of these single-nucleus traits as governed by the atomistic strain field gives rise to a unique fingerprint of the QD

FIG. 18. (Color online) Zeeman interaction having a unidirectional axis (left) versus QI with a bidirectional character (center). In actual QD samples the local major quadrupole axis is somewhat tilted because of shear strain with respect to magnetic field in Faraday geometry (right), which can accordingly reduce their competition.

FIG. 19. (Color online) Demonstration on a single $^{115}\text{In}$ nucleus the effects of various EFG parameter combinations on the CT (left) and ST (right) frequencies. The major EFG, $V_{ZZ}$ is in units of $3 \times 10^{21}$ V m$^{-2}$. The top row and middle left panel are for $\eta = 0.5$; middle left panel shows both $\eta = 0$ and $\eta = 1$ cases with the latter in dash-dotted lines; the bottom row is for $V_{ZZ} = -1$.

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