Average Local Order Parameter in Partially Ordered GaInP₂

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The application of a simple point-charge model to NMR spin echo measurements of ⁷¹Ga in random and partially ordered film of Ga₀.₅₂In₀.₄₈P provides the first quantitative and accurate estimate of the average degree of local ordering (average order parameter \( \eta \)) in a ternary III-V semiconductor. The value of \( \eta \) extracted is consistent with theoretical predictions. [S0031-9007(96)00441-3]

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Partial ordering of the mixed cation or anion sublattices in ternary III-V semiconductors has been the subject of intensive investigation for more than a decade [1]. In spite of these efforts there is currently no accurate and independent experimental measure of the parameter that is perhaps the most fundamental—the order parameter \( \eta \). (For various technical reasons, both electron and x-ray diffraction have difficulties providing a quantitative measure of \( \eta \) [2].) In Ga₀.₅₂In₀.₄₈P grown epitaxially on GaAs (hereafter referred to as GaInP₂) the specific ordering is the propensity of the cations (Ga and In) to form a Cu-Pt-type structure by segregating on successive cation \{111\} planes. The perfectly ordered structure of GaInP₂ is shown in Fig. 1. Samples made by liquid phase epitaxy (LPE) are completely disordered (random distribution of the Ga and In on the cation sublattice or \( \eta = 0 \)). On the other hand, samples made by organometallic vapor phase epitaxy (OMVPE) exhibit varying degrees of ordering depending on the preparation conditions.

Ordering has significant effects on many physical and electronic properties of GaInP₂. In particular, the optical band gap is reduced on ordering and the normally degenerate valence band is split. Band structure calculations have provided a relation between the degree of ordering and the reduction in the optical gap [3,4]. When compared with these theoretical calculations, various optical and modulated optical spectroscopies have been used to estimate \( \eta \) [5–7]. Values of \( \eta \) have also been inferred from transmission electron microscopy (TEM) [2] and from ⁷¹P NMR magic angle spinning experiments [8]. None of these techniques have as yet provided an accurate estimate of \( \eta \) that is independent of the band structure calculations.

In the present paper we report the use of ⁷¹Ga, ⁶⁹Ga, and ¹¹⁵In nuclear magnetic resonance (NMR) to provide an accurate measure of \( \eta \) in partially ordered GaInP₂. These measurements are independent of theoretical calculations of the band structure, and therefore they provide the first independent measurements of this important parameter in any partially ordered III-V semiconductor.

The random LPE sample studied in this work was grown on an [001] GaAs substrate using a graphite slider boat. Details are available elsewhere [9]. The partially ordered OMVPE sample was grown at atmospheric pressure on a 625 °C substrate using trimethylgallium, trimethyl...
indium, and phosphine in a hydrogen carrier gas. The substrates were [001] GaAs wafers misoriented 6° toward the [111] B direction. This sample has a band gap reduction similar to sample K-155 discussed in detail in Ref. [5]. Details of the growth are also available elsewhere [4]. Before performing the NMR measurements the substrates were either thinned by mechanical polishing or etched away using a mixture of 1:1 by volume 30% hydrogen peroxide and concentrated aqueous ammonia. This procedure resulted in approximately 10 mg of oriented material. NMR experiments were performed on a standard pulsed spectrometer at magnetic field up to 8.5 T. Pulse sequences of 90°-τ-24° or 90°-τ-65° were employed to produce the NMR echoes, and the typical 90° pulse widths employed were approximately 2.5 μs.

Figure 2 shows a representative 71Ga echo using a 90°-τ-65° pulse sequence for the LPE sample. Echoes for the OMVPE sample are similar. There are two distinct components to the echo in Fig. 2: a narrow echo (~4 μs) and a broad echo (~60 to 80 μs), whose exact widths and line shapes depend on the orientation of the magnetic field with respect to the crystallographic axes. The 69Ga and 115In echoes do not show any resolved structure. In the interest of brevity we will discuss exclusively the 71Ga results. Earlier measurements [10] on doping of isoelectronic elements into GaAs (In, for example) have established that the quadrupolar interaction between the quadrupole moment of the nucleus and the gradient of the magnetic field is essentially the same for both the CT and ST components, and they are independent of orientation. Values of the quadrupole coupling parameters. Plotting the amplitude as a measure of the linewidth, and hence of the quadrupole coupling parameters. 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are detected. In what follows we assume that the ratios plotted in Fig. 3 are proportional to the width of the ST echo.

To provide a quantitative measure of the average local order parameter $\eta$ we carry out a simple model calculation of the EFG at a Ga or In site by treating the lattice as an array of point charges [10,12]. The starting point for the model is atoms distributed on an undistorted zinc-blende lattice, but with different effective charges calculated for different atoms. Next we include relaxation [13] by allowing the P atoms neighboring each Ga or In to relax inward or outward 75% of the way to the bulk GaP or InP value. Finally, we calculate at each Ga or In site the EFG arising from the four nearest-neighbor P atoms, the charges and positions of which depend upon the distribution of second-nearest-neighbor Ga and In atoms. Using the bond polarity concept [14] for a Ga-P bond, the probability of finding the electron on the P nucleus is $(1 + \alpha_{GaP})/2$ while the probability of finding the electron on the Ga nucleus is $(1 - \alpha_{GaP})/2$ where $\alpha_{GaP} = 0.52$. The probabilities are similarly expressed for an In-P bond with $\alpha_{InP} = 0.58$. Since a P atom contributes five electrons to the valence band and has two-electron bonds with four cations, the total charge in units of $e$, $Z^*$, on a P ion is $Z^* = 5 - \sum_i (1 + \alpha_i) = 1 - \sum_i \alpha_i$. Denoting a P ion bonded to 4x Ga ions and $(1 - x)$ In ions by $P_{xGa}(1-x)In$, the charges on $P_{4Ga}$, $P_{3Ga1In}$, $P_{2Ga2In}$, $P_{1Ga3In}$, and $P_{4In}$ are $-1.08$, $-1.14$, $-1.20$, $-1.26$, and $-1.32$, respectively. Note that the charges are the same for every Ga and every In ion since each has four P neighbors. (Bulk values of $Z^*$ are used because they are essentially identical to those calculated for the alloy.)

To determine the positions of the ions we start with the “undistorted” GaAs lattice (GaInP$_2$ is lattice matched to GaAs) with Ga or In and P ions as the cations and anions, respectively. Thus all bonds are forced to be the same length ($2.360 \text{ Å}$). Next we keep the cation sublattice fixed and allow the P ions to adjust positions as suggested by extended x-ray absorption fine structure experiments on ternary III-V semiconductors [15]. The bonds are treated as springs whose natural lengths are the same as the bonds in the binary compounds. For simplicity the spring constants are assumed to be the same for both GaP and InP bonds. The positions of the P ions are then determined by balancing the elastic forces exerted on each P ion. Therefore, the position of each P ion is uniquely determined by its four Ga and/or In nearest neighbors. Note that in such a lattice the forces on the cations are not all balanced, but we ignore this higher order correction. We make the final simplification that only the nearest-neighbor P ions contribute to the EFG at a cation site. With these assumptions the EFG at a Ga site, for example, is completely determined by the 12 second-nearest-neighbor In and Ga atoms.

We label the second-nearest-neighbor shell configuratio by $q$, the positions of the nearest-neighbor P atoms in the unrelaxed lattice by $R_i$, the bond length of the unrelaxed lattice by $r_{q,i}$ ($i = 1, 2, 3, 4$), half the difference between the InP and GaP bond lengths by $\delta d = 0.09 \text{ Å}$, the Sternheimer factor by $\gamma_s$, the average charge on the five possible P sites by $Z_0 = -1.17$, and the charge on the nearest-neighbor P atoms by $Z_{q,i} (i = 1, 2, 3, 4)$. We further define the relative charge excess on a P atom by $z_{q,i} = (Z_{q,i} - Z_0)/Z_0$ and introduce the unit vectors $X_i = R_i/d$ and the nearly unit vectors $x_{q,i} = R_{q,i}/d$.

The EFG tensor at a Ga site can be written as

$$V_{q,\alpha\alpha} = \frac{Z_0(1 - \gamma_s)}{d^3} \sum_{i=1}^{4} \left[ z_{q,i}(3X_{i,\alpha} - 1) + 2\frac{\delta d}{d} (3X_{i,\alpha}x_{q,i,\alpha} - \vec{x}_{i} \cdot \vec{x}_{q,i}) \right],$$

(1)

$$V_{q,\alpha\beta} = \frac{3Z_0(1 - \gamma_s)}{d^3} \sum_{i=1}^{4} \left[ z_{q,i}X_{i,\alpha}X_{i,\beta} + \frac{\delta d}{d} (X_{i,\alpha}x_{q,i,\beta} - X_{i,\beta}x_{q,i,\alpha}) \right].$$

(2)

Note that the first term in each of the above two equations represents the contribution from the imbalance of the charges on the four nearest-neighbor P ions (charge effect).
and the second term represents the contribution from the displacement of the P ions from the unrelaxed positions (displacement effect). The coordinate system is define by $x = [110]$, $y = [1\bar{1}0]$, and $z = [001]$. From Eqs. (1) and (2) it can be shown that the displacement effect provides the dominant contribution to the angular dependence.

For any crystal orientation and second-nearest-neighbor configuratio the EFG tensor components can be calculated by proper rotation of the results of Eqs. (1) and (2), and the resulting linewidths can be calculated using the standard NMR expressions for quadrupolar broadened spectra. There are 4096 possible second-nearest-neighbor configuration and the probability for a particular configuratio to occur, $P_q$, is the product of 12 terms, one for each of the second-nearest-neighbor Ga or In atoms. Each term is either $0.5 + \eta/2$ or $0.5 - \eta/2$, where $\eta$ is the average local order parameter define above, depending on whether the $\{111\}$ plane is Ga or In rich and whether the second-nearest-neighbor is Ga or In. Assuming the ordering is uniform throughout the sample and that there is no ordering within the $\{111\}$ planes (no additional ordering besides the $\{111\}$ B ordering), $p_q$ can be calculated for each configuration for a given value of $\eta$. Because the Ga- and In-rich planes must be treated separately, the summation involves 8192 possible sites that are properly weighted for each value of $\eta$. In practice, just as some parameters in the model are calculated, so are the NMR linewidths due to the satellite transitions as indicated by the ratios shown in Fig. 3, we calculate the second moment $M$ of the NMR line shapes as obtained using the above procedure. (The square root of the second moment is proportional to the linewidth.) For the random case one can obtain an algebraic expression for the second moment $M \approx 48.4 - 23.2(4 \sin^2 \theta - 3 \sin^3 \theta)$, where $\eta > 0$ one can evaluate $M$ numerically. The solid line in Fig. 3(a) is the best fit of $M^{1/2}$ to the experimental data where a small isotropic broadening has been added to account for the fact that the LPE sample is slightly strained, probably due to incomplete lattice matching during growth. Since the displacement effect is the dominant contribution to the angular dependence, the calculations are not very sensitive either to the magnitude of the relaxation toward the binary lattice constants or to the magnitudes of the bond polarities.

Similar rotation patterns for $M^{1/2}$ can be calculated for selected values if $\eta$ and compared to the experimental data for the partially ordered OMVPE sample shown in Fig. 3(b). The best fit is obtained for $\eta = 0.6$ as shown by the solid line in Fig. 3(b). By least-squares analysis of the rotation patterns for different values of $\eta$ we estimate the error to be $\pm 0.05$. There are several possibilities for checking this value of $\eta$, such as actual line shapes for the CT echo, asymmetries in the CT and ST echoes, and so forth. These checks yielded values of $\eta$ consistent with that quoted above but they are less accurate. For example, a comparison of the CT line shapes for the LPE and OMVPE samples with those calculated for various values of $\eta$ confirms that the best fit are $\eta = 0.0^{+0.1}_{-0.0}$ and $\eta = 0.5^{+0.15}_{-0.25}$ respectively.

Theoretical arguments [3,4,16] suggest that the optical band gap reduction from the random alloy to the partially ordered alloy is proportional to $\eta^2$. In the partially ordered sample studied here the band gap reduction is $100 \pm 15$ meV (as measured using photoluminescence excitation spectroscopy at $\sim 5$ K) which, assuming $\eta = 0.6$, agrees with the theoretical prediction of Wei, Laks, and Zunger [4] within experimental error. This agreement shows that NMR may be used as a primary measurement of $\eta$ with which other secondary probes, such as optical band gap, can be calibrated.

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