Origin of the magnetic circular dichroism of absorption of the arsenic antisite in GaAs and Al\textsubscript{x}Ga\textsubscript{1-x}As

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We have investigated the transitions associated with magnetic circular dichroism of absorption (MCDA) in GaAs by studying the MCDA spectrum as a function of stoichiometry in Al\textsubscript{x}Ga\textsubscript{1-x}As grown at low temperatures via molecular-beam epitaxy. The main result of the stoichiometry-dependence study is that the spectrum of the singly ionized arsenic antisite can be well explained within the valence-band model, that is, the optical transitions are from the valence band to the A\textsubscript{1} ground state. The competing internal transition model can be refuted. The stoichiometry dependence also suggests that the observed diamagnetic spectrum of the neutral arsenic antisite could be linked to the zero-phonon line of the optical-absorption spectrum.

The singly ionized arsenic antisite, arsenic on a gallium site (As\textsubscript{Ga}\textsuperscript{+}), is a well-studied native defect found in GaAs, yet there is still an unresolved long-standing controversy associated with the defect’s optical spectra, especially the magnetic circular dichroism of absorption (MCDA) spectrum. A typical MCDA spectrum of bulk, semi-insulating GaAs is shown in Fig. 1. It consists of one negative peak at 0.94 eV and two positive peaks at 1.1 and 1.35 eV. In the past, two models, the internal-transition model\textsuperscript{1} and the valence-band-transition model,\textsuperscript{2} have been proposed to explain the MCDA spectrum of bulk semi-insulating (SI) GaAs.

According to Meyer, Spaeth, and Scheffler,\textsuperscript{1} in the internal-transition model, the MCDA arises from intracenter transitions from the A\textsubscript{1} ground state to two T\textsubscript{2} excited states of the defect, as seen in Fig. 2(a). This A\textsubscript{1} state is 0.52 eV above the valence band, and the two T\textsubscript{2} states are 1.05 and 1.29 eV above the A\textsubscript{1} states and are therefore resonant with the conduction band. The MCDA is then the superposition of two derivative peaks, caused by two so-called A\textsubscript{1} terms (finding their origin in the Zeeman splitting of the ground or excited states, see Ref. 3). Peaks due to the A\textsubscript{1} term are temperature independent, therefore the antisite related peaks should be temperature independent, contrary to the observed Curie law behavior (proportional to 1/T) of the MCDA spectrum.\textsuperscript{4,5} This already casts some serious doubts on the validity of the model proposed by Meyer, Spaeth, and Scheffler.

The valence-band transition model proposed by Kaufmann and Windscheif\textsuperscript{2} postulates that the two MCDA transitions of bulk GaAs are the photoneutralization transitions

\[ \text{As}_{\text{Ga}}^{\text{+}} + h\nu \rightarrow \text{As}_{\text{Ga}}^{\text{0}} + \text{hole}, \]

exciting a hole to the spin-orbit-split valence band, Fig. 2(b). Dipole transition selection rules are obeyed because of the s-like character of the A\textsubscript{1} ground state and p-like character of the valence band. The transitions are specifically to the heavy- and light-hole states of the \textGamma\textsubscript{8} valence band and to

![FIG. 1. The MCDA spectrum of As\textsubscript{Ga}\textsuperscript{+} in bulk Czochralski grown GaAs. The spectrum was collected at 1.8 K and under a 2 T magnetic field.](image)

![FIG. 2. (a) The internal excited-state model and (b) the valence-band model. See Refs. 1 and 2, respectively.](image)
the spin-orbit split-off band $\Gamma_7$. Thus, the hole transitions are from the ground state of the $\text{As}_{\text{Ga}}\text{Ga}^+$ defect to the valence-band states. Here the MCDA is explained as a superposition of three nonderivative $C_0$-term peaks. $C_0$-term peaks are caused by a Boltzmann distribution over the sublevels of the Zeeman-split ground state and are therefore temperature dependent, in line with the experimental data.\textsuperscript{4,5}

A study of the MCDA spectrum as a function of the change in band gap can clarify which physical model best explains the experimental data. There have been detailed investigations performed on both the excited and ground states of the $\text{As}_{\text{Ga}}\text{Ga}^+$ defect under pressure, a standard technique used to shift band gaps to higher energies. The knowledge of the change of levels and transitions as a function of pressure is summarized in Fig. 3. The ground state of the arsenic antisite is taken as the reference level. As can be seen in Fig. 3, pressure coefficients of the $\text{As}_{\text{Ga}}$ transitions observed in near-infrared absorption (NIRA) are 24.4 meV/GPa for the zero-phonon line (ZPL)\textsuperscript{6} and $-26.4$ meV/GPa for the broadband of the NIRA spectrum.\textsuperscript{6} Both transitions have the same initial $A_1$ state, but as demonstrated by the opposite shifts, they do not have the same final state. Von Bardeleben attributes the final state of the ZPL at 1.03 eV to the $T_2(1s)$ $L$ conduction-band state and the final state of the broadband to the excited $T_2$ antibonding state resonant with the conduction band.\textsuperscript{7} However, the assignment of the ZPL transition to the derived effective mass state of the $L$ band is at variance with the $T_d$ symmetry found in the detailed pressure studies of Kaminska, Skowronski, and Kusko.\textsuperscript{8} It has to be stated that the pressure dependence alone cannot support this important conclusion. Whether or not the transitions are indeed to the $L$ minimum or to a state derived from the entire conduction band, as suggested by Chadi and Chang for the $\text{DX}$ state,\textsuperscript{9} is irrelevant, as the pressure coefficient of such a mixed state would be very similar. In the current discussion we refer to it as the $L$-valley effective-mass state, for ease of reference. Taking into account the shifting $L$ conduction band, a 27 meV/GPa is obtained for an excitation from the $A_1$ state of the $\text{As}_{\text{Ga}}$ defect to an effective mass state of the $L$ conduction-band minimum. This is indeed close to the one determined for the ZPL, 24.4 meV/GPa. The internal transition to the $T_2$ state shows an overall decrease in energy ($-10$ meV/GPa calculated, $-26.4$ meV/GPa measured). Along with the shifts observed for the excited states, it is also deduced that the valence band shifts at a rate of $-28$ meV/GPa, i.e., away from the $A_1$ level.\textsuperscript{8,9,10,11} Consequently, an optical transition from the ground state of the defect to the valence band should shift to higher energies, 28 meV/GPa. Thus, the internal-transition model requires the MCDA bands to shift to lower energies as the band gap increases, while the valence-band model requires the bands to shift to higher energies. Hence, a pressure-dependence study of the MCDA spectrum can discriminate between the two models.

Instead of pressure, one can also use stoichiometry to change the level positions, i.e., replace some of the Ga atoms with Al to form $\text{Al}_{x}\text{Ga}_{1-x}\text{As}$. High-pressure effects correlate well with effects induced by alloying. We use the relation 1 GPa is equivalent to 7.7% Al-mole fraction, as derived from Fig. 1 of Ref. 12 and Fig. 1 of Ref. 13. Indeed, values found by Menéndez et al.\textsuperscript{16} show that, for instance, the valence band of $\text{Al}_{x}\text{Ga}_{1-x}\text{As}$ shifts $-4$ meV/% Al with alloying\textsuperscript{11} with respect to vacuum (while the $L$, $\Gamma$, and $X$ conduction bands shift approximately 7.5, 2, and 3.75 meV/% Al, respectively\textsuperscript{15}), which is similar to the $-3.6$ meV/% Al as derived from the correlation between pressure and alloying.

Transient capacitance spectroscopy on metal-organic chemical-vapor deposition grown $\text{Al}_{x}\text{Ga}_{1-x}\text{As}$ by Johnson et al.\textsuperscript{16} indicates that the energy position of the ground state of the antisite defect shows a remarkable horizontal alignment with respect to the vacuum as Al-mole fraction increases. This horizontal alignment is also observed by Silberberg, Omling, and Samuelson\textsuperscript{17} for the $\text{As}_{\text{Ga}}$ defect in GaAs$_{1-x}$P$_x$. Thus, both cases of alloying indicate that the ground state of the antisite does not shift in energy position with alloying. For this reason, we have also taken the antisite level horizontal as a function of alloy composition. Therefore, the shift of the valence band with respect to the ground level of the antisite translates to $-4$ meV/% Al, as measured by Menéndez et al.\textsuperscript{14} Furthermore, photoquenching studies of the 1.18- eV NIRA transition to the excited $T_2$ level in both GaAs$_{1-x}$P$_x$ and Al$_{1-x}$Ga$_x$As show that the excited state of the $\text{As}_{\text{Ga}}$ defect also does not shift with alloying.\textsuperscript{18} From these past investigations of the $\text{As}_{\text{Ga}}$ defect it can be deduced that both the ground and excited energy levels are independent of alloying.

Hence, we can conclude that in the valence-band model a peak shift of $+4$ meV/% Al is expected, and in the internal-transition model a peak shift of $-3.4$ meV/% Al is expected if the pressure data can be extrapolated to alloy composition, or no shift is expected if alloying data are considered directly.

To address this issue, we have studied the MCDA spectra of $\text{Al}_{x}\text{Ga}_{1-x}\text{As}$ grown at low temperatures via molecular-beam epitaxy (LT $\text{Al}_{x}\text{Ga}_{1-x}\text{As}$). The LT material was chosen because of the high As antisite defect concentration: $19,20 [\text{As}_{\text{Ga}}^\text{As}]=10^{20}$ cm$^{-3}$ and $[\text{As}_{\text{Ga}}^\text{Ga}]=5\times10^{19}$ cm$^{-3}$. The samples used for this study were grown on either $n^+$ or SI GaAs in a Varian Modular Gen II MBE chamber at 230 °C. The LT layers with an Al-mole fraction ranging from $x$
Valence-band model, but it has the correct sign and similar magnitude. For the internal-transition model, either a negative shift, or at best no shift, would need to be observed. When deciding between the two models, the valence-band transition of the minimum is plotted, although a derivative line shape still cannot be excluded. For the present analysis, we used the minimum position given for the diamagnetic peak. As seen in Figs. 4 and 5, the diamagnetic peak shifts to higher energies because it is linked to a part of the valence band \((d_{x^2-y^2}^\downarrow-L_4^\downarrow)\) that is, in GaAs, slightly set off from the other band maximum \((\Gamma_8^\downarrow-L_9^\downarrow)\). Because this offset is absent in AlAs\((\Gamma_{15}^\downarrow-L_7^\downarrow)\), the two peaks [transitions 2 and 3 in Fig. 2(b)] should overlap in AlAs. Evidently, the first peak must then move faster than the second peak. Following this line of reasoning, we can predict that the theoretical MCDA spectrum in AlAs should consist of only two peaks.

The experimental data on LT Al\(_2\)Ga\(_{1-x}\)As also raise an interesting issue for the diamagnetic peak. Previously, the diamagnetic peak was assigned to the broadband observed in the NIRA at 1.18 eV due to similar quenching, linewidth, and line position.\(^5\) Figure 6 shows the spectrum for LT-GaAs after the subtraction of the paramagnetic spectrum. A derivative of a Gaussian line shape fits best to the experimental data of the diamagnetic spectrum. Indeed, we expect a derivative line shape for a diamagnetic \(A_1\)-term in MCDA. The data are not conclusive, though, since the spectrum cannot be measured beyond 1.45 eV (because of band-to-band absorption) and, consequently, a substantial part of the derivative peak is missing. Therefore, a normal line shape still cannot be excluded. For the present analysis, we used the minimum of the peak. It has to be noted that to find the positions of the derivative peak, approximately 0.19 eV should be added. See the text and Fig. 6.
that this MCDA absorption might be associated with the ZPL observed in NIRA. As discussed above, the ZPL has been associated with the \( L \) valley\(^7\) and the \( L \) valley shifts at a rate of approximately 3.5 meV/\% Al.\(^10\)-\(^12\) The observed shift of the diamagnetic peak therefore substantiates this assumption. This would then be the first time the phonon-broadened peak of the ZPL is observed. The large splitting (\( \Delta E \)) between the ZPL (1.04 eV) and the maximum of the band (1.193 eV), though, would imply a large Huang-Rhys factor (\( S = \Delta E/\hbar \nu = 14 \), assuming a phonon energy \( \hbar \nu = 11 \) meV, and even much larger if the line shape is a derivative). For such large lattice relaxation the ZPL should hardly be visible. Therefore, it cannot yet be ruled out that this MCDA peak is due to another, hitherto unknown excitation of the diamagnetic \( \text{As}_{\text{Ga}}^0 \).

Concluding, we have shown that the original paramagnetic MCDA spectrum of \( \text{As}_{\text{Ga}}^+ \) cannot be explained in the framework of the internal-transition model. The valence-band model better describes the stoichiometry-dependence data, predicting correctly both the sign and magnitude of the shift. Also, we observed a new band of the \( \text{As}_{\text{Ga}} \) that might be the broadband of the ZPL or an independent diamagnetic transition of this defect.

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