Conduction band effective masses have been measured for the first time by cyclotron resonance in Ga$_x$In$_{1-x}$As alloys, as a function of alloy composition. These measurements were made on high-purity epitaxially grown crystals, ranging in alloy concentration from 100 to 84.6% GaAs, using submillimeter laser sources at 119 and 337 μm. The values obtained for the band edge effective masses are consistently heavier than predicted from $k$-$p$ perturbation theory.

Ga$_x$In$_{1-x}$As ALLOYS have become increasingly important for infrared detectors and optically pumped lasers. Studies of the fundamental band gaps and electron effective masses of this alloy system have been made in the near infrared. However, the effective masses determined from these measurements are only accurate to about 10%. New high purity homogeneous epitaxial material has enabled us to apply the precise techniques of electron cyclotron resonance utilizing submillimeter lasers to this problem. These measurements, made for the first time on an alloy as a function of composition, reveal masses which are consistently heavier than have been predicted.

The single crystalline material used in these measurements was epitaxially grown on semi-insulating GaAs and ranged in alloy composition from 100 to 84.6% GaAs. The samples were characterized by electron microprobe analysis, photoconductivity, resistivity and Hall measurements with the relevant data summarized in Table 1. The mobility values indicate that the quality of the material deteriorated with increasing indium content.

### Table 1. Fundamental band gap $E_g$, mobility $\mu$, and net carrier concentration $n_D - n_A$, for Ga$_x$In$_{1-x}$As alloys studied by cyclotron resonance. Samples were typically 50 microns thick.

<table>
<thead>
<tr>
<th>GaAs (%)</th>
<th>$n_D - n_A$ /cm$^3$</th>
<th>$\mu_{77,K}$</th>
<th>$E_g$ 300°K (microns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>$1.29 \times 10^{14}$</td>
<td>171,634</td>
<td>0.88</td>
</tr>
<tr>
<td>97.9</td>
<td>$2.3 \times 10^{14}$</td>
<td>72,000</td>
<td>0.90</td>
</tr>
<tr>
<td>96.0</td>
<td>$3.0 \times 10^{14}$</td>
<td>45,000</td>
<td>0.92</td>
</tr>
<tr>
<td>93.3</td>
<td>$1.5 \times 10^{15}$</td>
<td>26,700</td>
<td>0.96</td>
</tr>
<tr>
<td>89.5</td>
<td>$2.5 \times 10^{15}$</td>
<td>12,000</td>
<td>1.00</td>
</tr>
<tr>
<td>84.6</td>
<td>$3.1 \times 10^{15}$</td>
<td>16,500</td>
<td>1.07</td>
</tr>
</tbody>
</table>

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† Also Lincoln Laboratory, MIT.
Each of our alloy crystals was immersed in liquid helium at 4.2°K and located in the Faraday configuration in the bore of a 100 kG superconducting magnet. Cyclotron resonance generated by cw millimeter sources at 337 and 11942 (principally the latter) was observed as a peak in photoconductive response of the crystal or as a minimum in transmitted intensity as the magnetic field was varied. NMR measurements in Al were used to determine the magnetic field to an accuracy of better than 0.05%. In all cases the precision of our measurements was limited by uncertainties in locating the resonance.

To correct our experimental cyclotron resonance results to band edge effective masses, we consider non-parabolic effects arising from the interaction of the conduction band with the nearest valence band and the split-off band. This interaction reduces the energy of the nth Landau level from its unperturbed value of \( (n + 1/2) \hbar \omega_c \) to the value

\[
E_n = \frac{\hbar e H}{m^*(0)c} \left( E_g + \Delta_0 \right) \left( n + \frac{1}{2} \right)
\]

\[
+ \frac{1}{2} B_d\, \omega_c \left( 0 \right) H \left( \frac{E_g + \Delta_0}{\Delta_0} \right) \left( \frac{1}{E_n + E_g} - \frac{1}{E_n + E_g + \Delta_0} \right)
\]

Here \( E_n \) is the energy of the \( n \)th Landau level, \( E_g \) is the energy gap and \( \Delta_0 \) is the valence band spin–orbit splitting. Only the transition \( E_g + \Delta_0 \) is considered, since the quantum limit conditions \( \hbar \omega_c > kT \) and \( \hbar \omega_c > E_F \) are well satisfied for these samples.

The curve (a) in Fig. 1 which lies consistently below the data points is the variation in band edge effective mass as determined from \( k \cdot p \) perturbation theory and the experimentally measured energy gaps. \( k \cdot p \) perturbation theory provides reasonably good results for the conduction band effective masses in binary III–V compounds even when the interacting bands are restricted to only the \( \Gamma_1 \) valence band and the \( \Gamma_5 \) spin–split valence band. In this approximation the effective mass \( m^* \) is given by

\[
\frac{m_0}{m^*} = 1 + \frac{P^2}{3} \left( \frac{2}{E_g} + \frac{1}{E_g + \Delta_0} \right)
\]

where \( m_0 \) is the free electron mass, \( E_g \) is the fundamental gap and \( \Delta_0 \) is the valence band spin–orbit splitting. \( P^2 \), the square of the intraband matrix element, varies only slightly among the III–V compounds. If we use the experimental values \( m^* = 0.0665 m_0 \), \( E_g = 1.42 \text{ eV} \), and \( \Delta_0 = 0.33 \text{ eV} \) for GaAs, equation (2) gives \( P^2 = 22.7 \). The corresponding values \( m^* = 0.0230 m_0 \), \( E_g = 0.35 \text{ eV} \), and \( \Delta_0 = 0.44 \text{ eV} \) yield \( P^2 = 21.5 \), for InAs. Since homogeneous alloy material exhibits all the band features of the constituent compounds, \( 2-8 \) it is reasonable to
The fundamental energy gap in Ga$_{1-x}$In$_x$As alloys is known to vary nonlinearly with alloy composition. Recent work indicates that the equation

$$E_g(x) = 0.35 + 0.48x + 0.59x^2$$

gives a good description of the variation of energy gap ($E_g$) vs. GaAs composition ($x$) in this alloy system. The energy gap measurements made on the samples used in the cyclotron resonance studies (Table 1) are in good agreement with equation (3). The value of $E_g$ is a slowly varying function of alloy composition and furthermore is not a sensitive parameter in determining $m^*$ in equation (2), especially for the GaAs-rich alloys that were studied here. Thus, the predicted variation of band edge effective mass with alloy composition, curve (a) in Fig. 1, exhibits nearly the same non-linearity as the fundamental energy gap. 

Errors associated with this curve arise from uncertainties in the variation of $E_g$, $\Delta_0$, and $P^2$ with alloy composition. Over the range studied, i.e. from $x = 1$ to $x = 0.846$, we estimate these errors could produce at most a two per cent variation in the curve. Comparing the experimentally determined band edge effective masses with curve (a) reveals a shift to heavier mass with increasing InAs content (for example, the effective mass of the 84.6% GaAs alloy is 5.9% heavier than predicted). This difference is well beyond the expected errors indicated above. As a reference line for Fig. 1, curve (b) shows a linear variation of effective mass with alloy composition. This curve appears to give an excellent fit to the experimental data.

Before discussing possible causes of the heavier masses we have observed, several sources of systematic error must be considered. Since the alloys were grown on GaAs substrates, errors in the effective masses could arise from alloy compositional grading near the substrate-layer interface or from lattice-mismatch induced plastic strain throughout the layer. Significant compositional grading would result in a GaAs-rich region near the interface which should produce a broadening of the cyclotron resonance on the high magnetic field side. Since there are no discernible asymmetries in our cyclotron resonance lineshapes, the effects of grading must be small. Similarly, lattice-mismatch induced strain does not appear to account for our results. The first order effect of this strain on the masses occurs through a shift of the fundamental band gap. Since experimental values of the gap are employed throughout our calculations, this effect should be virtually eliminated.

The heavier effective masses therefore indicate real discrepancies with predicted results for this alloy system. It must be noted that it is difficult to calculate the conduction band effective mass at this energy ($= 10$ meV) above the band edge to the level of precision of these measurements. Even in GaAs there are indications that simple $k\cdot\!p$ perturbation theory is not totally adequate. For example, when we use the standard six band model for calculating nonparabolicity, our cyclotron resonance measurements in GaAs at 337 and 119 $\mu$ yield band edge masses which differ by 0.5% (or roughly 30% of the non-parabolic correction). Also, equation (1) predicts a splitting of the cyclotron resonance line at 119 $\mu$ for spin-up and spin-down transitions. This has been observed in GaAs and is shown in Fig. 2. Although the separation of spin-up and spin-down cyclotron resonance is only 150 G, the two peaks are well resolved. This splitting is about three times the predicted separation using a $g$-value of 0.5 and the six-band model.

![Fig. 2. Spin-down and spin-up Landau level transitions in GaAs split by non-parabolicity. Bias = 70 nA.](image)
These results imply that a more complete treatment of interacting bands is necessary. Nevertheless, the increase in band edge effective mass for the alloys, especially those richest in indium, is greater than that which could reasonably be accounted for by including additional bands in the $\tilde{k}$-$\tilde{p}$ calculation. Our results suggest that the heavier masses arise from a unique property of the alloy, perhaps interaction of the Landau levels with the particular phonons characteristic of the Ga$_x$In$_{1-x}$As system. We are currently extending our measurements in these alloys to higher frequencies (79 and 84 $\mu$) in order to further probe the origins of observed deviations from theory.

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REFERENCES

18. The 93.3 and 84.6% GaAs alloys were intentionally graded (the graded regions were 18% of the total layer thickness). No systematic variations of effective mass are observed between the two types of samples.
19. Evidence that this is indeed the spin-splitting comes from the temperature dependence of the relative intensity of the two lines between 4.2 and 2.0$^\circ$K.