Classical and quantum conductivity in $\beta$-Ga$_2$O$_3$

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The conductivity $\sigma$, quantum-based magnetocconductivity $\Delta \sigma = \sigma(B) - \sigma(0)$, and Hall coefficient $R_H (= \mu_B/\sigma)$ of degenerate, homoepitaxial, (010) Si-doped $\beta$-Ga$_2$O$_3$, have been measured over a temperature range $T = 9$–320 K and magnetic field range $B = 0$–10 kG. With ten atoms in the unit cell, the normal-mode phonon structure of $\beta$-Ga$_2$O$_3$ is very complex, with optical-phonon energies ranging from $kT_{po} \approx 20$–100 meV. For heavily doped samples, the phonon spectrum is further modified by doping disorder. We explore the possibility of developing a single function $T_{po}(T)$ that can be incorporated into both quantum and classical scattering theory such that $\Delta \sigma \propto B$, $\Delta \sigma \propto T$, and $\mu_B \propto T$ are all well fitted. Surprisingly, a relatively simple function, $T_{po}(T) = 1.6 \times 10^3[1 - \exp(-(T + 1)/170)]$ K, works well for $\beta$-Ga$_2$O$_3$ without any additional fitting parameters. In contrast, $\Delta \sigma \propto T$ in degenerate ScN, which has only one optical phonon branch, is well fitted with a constant $T_{po} \approx 550$ K. These results indicate that quantum conductivity enables an understanding of classical conductivity in disordered, multi-phonon semiconductors.

The semiconductor Ga$_2$O$_3$ has five structural forms, $\alpha$, $\beta$, $\delta$, and $\epsilon$, the most stable of which is $\beta$-Ga$_2$O$_3$ (hereafter called $\beta$GAO), which crystallizes in the monoclinic form. This material has experienced extensive research activity in the last few years, mainly because of its high band gap, $E_g \approx 4.6$–4.9 eV, significantly higher than that of most other common wide-band-gap semiconductors, such as GaN, ZnO, and SiC. This feature leads to a higher breakdown field, important for power electronics, and also less absorption in the UV, useful for applications requiring transparency. Moreover, even with this large band gap, $\beta$GAO can be highly doped with shallow donors such as Si and Sn, attaining free-electron concentrations $n \approx 2 \times 10^{20}$ cm$^{-3}$. Such high concentrations enable transparent electrodes for photovoltaics and flat-panel displays, and regrown ohmic contacts. Finally, homoepitaxial device technology is possible because large $\beta$GAO crystals can be grown by several different techniques.

With such interesting practical applications on the horizon, it is important to understand the classical electrical properties, in particular, conductivity $\sigma$, concentration $n$, and Hall mobility $\mu_H = \sigma R_H$, where $R_H$ is the Hall coefficient. For binary semiconductors with only two atoms in the unit cell, such as GaN, SiC, ZnO, and ScN, the relevant scattering theory is simplified by the existence of only one branch of optical phonons. Thus, polar-optical-phonon scattering in these materials can be effectively described in terms of only one longitudinal optical phonon, of energy $kT_{po}$, where $k$ is Boltzmann’s constant and $T_{po}$ is the polar optical phonon temperature. (For reference, the table on p. 84 of lists $T_{po}$ values for sixteen binary semiconductors.) In contrast, $\beta$GAO contains ten atoms in the unit cell and thus nine branches of optical phonons, greatly complicating the analysis. The full spectrum of normal-mode phonons has recently been calculated and discussed in detail. However, in this study, we will be concerned with degenerate Si-doped $\beta$GAO, which has the additional complication of disorder due to the random positions of the Si-dopant atoms. Such disorder leads to small, negative contributions to the conductivity via a quantum effect, electron-wave constructive interference. This effect can be reduced by an increase in temperature $T$ or magnetic-field strength $B$, with the latter leading to a positive magnetocconductivity (MC). We define $\Delta \sigma(B,T) = \sigma(B,T) - \sigma(0,T)$, and will show that a theoretical analysis of $\Delta \sigma$ as a function of $B$ and $T$ provides enough detail of the actual phonon spectrum to quantitatively explain $\mu_B \propto B$, a completely different experiment. Besides this positive contribution to the MC, a much more common, non-quantum, negative contribution to the MC can also exist, however, it is Negligible in our sample due to a high degree of degeneracy.

The film of this study was homoepitaxial, grown by pulsed laser deposition (PLD) at 550°C on a Fe-doped (010) $\beta$GAO substrate. The substrate was semi-insulating and thus electrically isolated from the film. The growth temperature was 5% O$_2$/95% Ar gas mixture at 1.33 Pa, and the ablation target was a 99.99% pure sintered Ga$_2$O$_3$
A film thickness $d = 502 \text{ nm}$ was measured by contact profilometry. The thickness was also determined from spectral reflectance $R_m$ and transmittance $T_m$ measurements which can be accurately converted to the elements $\eta$ and $\kappa$ of the index of refraction ($\eta + i\kappa$) in a homoepitaxial sample\(^\text{15}\). At an energy $E = 2 \text{ eV}$, $\eta = 2.02$, and Fabry-Perot oscillations (FPO) then yielded $d = 508 \text{ nm}$, close to the profilometer value. Another common use of $R_m$ and $T_m$ measurements is determination of the band gap $E_g$\(^\text{15}\). The values of $\eta$ and $\kappa$ can be directly converted to absorption $\alpha$ and reflection $R$ coefficients, and for crystalline materials with a direct band gap, a plot of $\alpha^2$ vs energy $E$ will have an intercept $E_g$ at $E = 0$. As shown in Fig. 1, the result is: $\alpha^2 = 5 \times 10^{11} (E - 4.57 \text{ eV}) \text{ cm}^{-2}$, giving $E_g = 4.57 \text{ eV}$. In agreement, typical $E_g$ values for $\beta$-GaO mentioned in the literature are 4.5–4.9 eV\(^\text{1}\).

Measurements of sheet carrier concentration $n_s$, sheet conductance $\sigma_s$, and sheet Hall coefficient $R_{Hs}$ were carried out in a LakeShore 7507 Hall-effect system over a temperature range $T = 9–320 \text{ K}$ and a magnetic-field range, $B = 0–10 \text{ kG}$. (All of the numbered equations in this work are in MKS units. However, in the text we will report $B$ in “kG” rather than in the MKS unit “T” because “T” is already used for temperature. Note that $10 \text{ kG} = 1 \text{ T}$.)

For comparison with theory, $\sigma_s$ was converted to conductivity $\sigma = \sigma_s/d$, $R_{Hs}$ to volume electron concentration $n = (edR_{Hs})^{-1}$, and Hall mobility to $\mu_H = \sigma R_{Hs}$\(^\text{14}\). Plots of $n$, $\mu_H$, and $\sigma$ vs $T$ are shown in Fig. 2. (Note that because $n$ is nearly constant at $1.2 \times 10^{20} \text{ cm}^{-3}$, the layer is degenerate, and the so-called “Hall factor” is thus close to unity; in such a case, $n$ is the true carrier concentration\(^\text{14}\).)

In Fig. 2, we have plotted $\sigma$ at both $B = 0$ and $B = 10 \text{ kG}$. Although the curves appear to be nearly identical on the scale of this plot, their small difference $\Delta \sigma$ is important and is expanded and plotted vs temperature in Fig. 3.
As mentioned earlier, the β-GAO unit cell has 10 atoms that generate 30 normal modes of vibration, 3 acoustic and 27 optical\(^6\). In this work we will be concerned with the effects of these phonons on conductivity. Acoustic phonons scatter electrons elastically, or nearly so, and can affect \(\mu\) in degenerate semiconductors at low temperatures\(^4\). However, they will have negligible effect on electron phase and thus will not influence \(\Delta\sigma\). Optical phonons, on the other hand, lead to inelastic scattering and will have a strong effect on \(\Delta\sigma\)\(^1\). They will also affect \(\mu\), but only at higher temperatures because temperature-independent ionized-impurity scattering, an elastic process, is much stronger than phonon scattering at low temperatures in highly-doped materials.

The random positions of the Si ions lead to a disorder that can result in a partial localization of the phonon and electron structures, known sometimes as “weak localization”\(^1\). Indeed, this disorder is the origin of the \(\Delta\sigma\) measured here. To first order, it is customary to express the altered phonon spectrum as a somewhat localized superposition of the normal modes\(^1\). In the spirit of that approximation, our approach here will be to find an effective value of \(T_{po}\) at each temperature, i.e., \(T_{po}(T)\), that can correctly describe optical-phonon scattering in three independent experiments: \(\Delta\sigma\) vs \(T\), \(\Delta\sigma\) vs \(B\), and \(\mu\) vs \(T\).

Transport in both bulk and thin-film β-GAO has been studied by several groups in the recent past\(^8,10,16,17\). Ma et al.\(^16\) demonstrated the critical mobility-limiting role of polar-optical phonons by analyzing \(\mu\) vs \(T\) at \(n \sim 10^{18}\) cm\(^{-3}\), and also \(\mu\) vs \(n\) at \(n \sim 10^{18}–10^{19}\) cm\(^{-3}\) and at \(T \sim 77\) K and 300 K. Among other things, they found that an effective value of \(kT_{po} \approx 44\) meV (511 K) gave a reasonable fit to a compilation (literature) of \(\mu\) vs \(n\) data at 300 K. Also, in bulk, nondegenerate β-GAO, Oishi et al.\(^8\) found that the high-temperature mobility is controlled by a single effective \(T_{po}\) although its value was unspecified\(^17\). Finally, Ghosh and Singisetti carried out a rigorous calculation of \(\mu\) vs \(T\) for an ordered, nondegenerate sample with \(n \sim 10^{17}\) cm\(^{-3}\), and theory agreed well with experiment\(^8\). They included the effects of all the individual optical phonons and found that phonons of different energies and polarizations affected the scattering in different ways at different temperatures. For example, an optical phonon of energy \(\approx 21\) meV (\(T_{po} \approx 244\) K) dominated the mobility at 300 K\(^8\). At lower temperatures, other optical phonons became important and of course it was also necessary to add the scattering contributions of acoustic phonons and ionized impurities. In another theoretical work, Kang et al.\(^10\) performed first-principles calculations on the electron and phonon structures and also calculated scattering rates and mobilities. In agreement with the conclusions of Ghosh and Singisetti\(^8\), they showed that many phonons contribute to the scattering. Moreover, they pointed out the dominance of polar vs nonpolar optical scattering and showed that, contrary to other assertions, the mobility does not have a large anisotropy. In principal, detailed and rigorous calculations such as those described above could be carried out for all lightly-doped, ordered β-GAO samples; however, the disorder arising from heavily-doped samples will modify the actual phonon spectrum and require a more complicated analysis\(^15\).

We first consider the classical theory of \(\mu\) vs \(T\) in degenerate semiconductors, standard in the literature\(^1\) except for the treatment of optical-phonon scattering. (In the equations below, the effective mass \(m^*\), static dielectric constant \(\varepsilon_0\), and high-frequency dielectric constant \(\varepsilon_1\) were taken from ref.\(^1\).) and the acoustic deformation constant \(E_0\) and longitudinal elastic constant \(c_l\) from ref.\(^15\), noting that \(c_l = \rho_d n_s^2\), where \(\rho_d\) is the mass density and \(n_s\) is the speed of sound. The only fitted parameter in our study is \(T_{po}\). For degenerate materials, the dominant scattering mechanisms are typically ionized impurities (“ii”), acoustic phonons (“ac”), and optical phonons (“po”). The existence of degeneracy greatly simplifies the calculations, because all scattering basically occurs at one energy, the Fermi energy, \(E_F = (\hbar^2/2 m^*)(3\pi^2 n)^{2/3}\), where \(\hbar\) is the reduced Planck’s constant. For degenerate electrons, Matthiessen’s Rule\(^14,18\) applies exactly:

\[
\mu(n, N_D, N_A, T) = \left[\mu_{ii}(n, N_D, N_A)^{-1} + \mu_{ac}(n, T)^{-1} + \mu_{po}(n, T)^{-1}\right]^{-1}
\]

We will assume that the dominant donor has charge \(Z_D\), and the acceptor, \(Z_A\); then \(n = Z_D N_D - Z_A N_A\). In our case, the dominant donor is the dopant SiGa, with \(Z_D = 1\). The form of Eq. 1 assumes that a relaxation time \(\tau\) can
be defined for each scattering mechanism, i.e., \( \mu = e\tau/m^* \). This criterion holds for elastic scattering (ii and ac) but not necessarily for inelastic scattering (po), discussed further below. From the degenerate Brooks-Herring ionized-impurity scattering theory\(^{14} \), \( \mu_i \) can be written

\[
\mu_i(n) = \frac{24\pi^3}{e^2m^*} \frac{1}{\left(\ln(1 + y(n))\right)^{1/2}} \frac{n}{Z^2 N_{ii}}
\]

(2)

where \( Z^2 N_{ii} = N_{ii,\text{eff}} = Z_o^2 N_i + Z_A^2 N_A \), where \( N_{ii,\text{eff}} \) is the effective concentration of ionized impurities\(^{18} \). [Note that \( N_{ii,\text{eff}} \) is the only fitted parameter in Eq. 2, and from it we can calculate \( N_D \) and \( N_C \): \( N_D = (N_{ii,\text{eff}} + nZ_o)/(1 + Z_o) \) and \( N_C = (N_{ii,\text{eff}} - n)/(1 + Z_A) \).] In Eq. 2, \( y(n) \) can be written\(^{14} \)

\[
y(n) = \frac{3^{1/3}4\pi^{8/3}e^2n^{1/3}}{e^2m^*}
\]

(3)

The other two scattering terms in Eq. 1 are:

\[
\mu_{ac}(n, T) = \frac{\pi\hbar^2 c_i}{2^{1/2}(m^*)^{3/2}E_i\varepsilon^2} (\varepsilon_{n})^{1/2} = \frac{\pi^{1/2}\hbar^2 c_i}{3^{1/3}m^*E_i\varepsilon^2} T^{1/3}T_B
\]

(4)

\[
\mu_{po}(T) = \frac{4\pi\varepsilon_0(3\pi)^{1/2}\hbar^2 n^{1/3}T^{1/3}\sinh^3\left(\frac{T}{2}\right)}{e^2T_{po}^{2}(m^*)^{3/2}(\varepsilon_{n}/\varepsilon_{11} + 1)}
\]

(5)

Equation 4 is well-known\(^{14} \), but Eq. 5 is not in the literature, to our knowledge. To derive Eq. 5, we begin with Eq. 17 in the theoretical paper of Howarth and Sondheimer (HS). These authors use a variational theory to show that even for polar optical phonon scattering a relaxation time \( \tau \) can be defined for each scattering mechanism, i.e.,

\[
\tau = \frac{e^2}{2\pi^2\hbar} \sum_{N_o=0}^{\infty} \frac{2((N + 1 + \delta(B, T))^{1/2} - (N + \delta(B, T))^{1/2})}{} - \frac{1}{(N + 1/2 + \delta(B, T))^{1/2}}
\]

(6)

where \( e^2/2\pi^2\hbar = 1.23 \times 10^{-5} \text{S} \), is the so-called unit of quantum conductance. Also, \( I(B) = (h/eB)^{1/2} \) and

\[
\delta(B, T) = \frac{T^2(B)}{4\tau_{po}(T)D(T)} = \frac{3e}{4h(3\pi^2 n^{21})}\mu_{po}(T)\mu(T)B
\]

(7)

where \( \tau_{po} \) is the inelastic-scattering relaxation time and \( D(T) \) is the diffusion coefficient. We have modified Eq. 7 by setting \( \tau_{po} = m^*\mu_{po}/e \) and \( D = \nu_e^2/3 = \hbar^2/(3\pi^2 n^{21})\mu/3e m^* \), where \( \mu_{po} \) is given by Eq. 5 and \( n \) and \( \mu \) are measured quantities. A remarkable consequence of Eq. 6 occurs in the limit of low T (which gives high \( \mu_{po} \)) and large B which renders \( \delta \ll 1 \) and
This result is independent of temperature or any material parameter!

Equation 6 is applied to experimental results for \( \beta \mathrm{GAO} \) in Fig. 3, which displays \( \Delta \sigma \) vs T at \( B = 10 \text{ kG} \). It is instructive to compare the same function in thin-film, degenerate ScN. Note that ScN has only two atoms per unit cell and thus only one optical branch, which can be represented by a single value of \( T_{po} \). As seen in Fig. 3, the value \( T_{po} = 550 \text{ K} \) fits the ScN data very well. (A more detailed study of magnetoconductance in ScN will be presented elsewhere.) However, a single \( T_{po} \) is not sufficient for \( \beta \mathrm{GAO} \), and indeed, we find the required \( T_{po} \) at a given T, by solving Eq. 6 as a transcendental equation with \( T_{po} \) as the unknown. The resulting points \( T_{po} \) vs T are plotted in Fig. 4, and they can be reasonably well fitted by the relatively simple function

\[
T_{po}(T) = 1.6 \times 10^3 \left[ 1 - \exp \left\{ -\frac{1}{170} \right\} \right] \text{K}
\]

This equation can then be further tested via an independent experiment, \( \Delta \sigma(B, T) = \sigma(B, T) - \sigma(0, T) \) vs B, \( B = 0 - 8 \text{ kG}, T = 9, 15, 20, \) and \( 25 \text{ K} \). (For this particular experiment, 8 kG was the maximum field that could be used.) As seen in Fig. 5, the fit is excellent for \( T = 9, 15, \) and \( 20 \text{ K} \), and acceptable for \( T = 25 \text{ K} \), where the signal is rapidly decreasing due to inelastic scattering.

The final test of \( T_{po}(T) \) is its applicability in a third independent experiment, \( \mu_H \) vs T, illustrated in Fig. 2. Here we apply Eqs 1–5, comparing three choices of \( T_{po} \) in Eq. 5: \( 1000 \text{ K}, 1400 \text{ K} \), or our derived function \( T_{po}(T) \). The first two values were chosen to bracket the potential fits attained with \( T_{po} \) constant; however, neither is satisfactory, nor is any other constant value. On the other hand, the function \( T_{po}(T) \) works very well. We are now left with only one unknown in Eqs 1–5, \( N_{ii,eff} \), which turns out to be \( 5.97 \times 10^{20} \text{ cm}^{-3} \) from the solid-line fit shown in Fig. 2. We know that the dominant donor concentration \( N_D = [\text{Si}_{Ga}] \), and we can speculate that the dominant acceptor is the Ga vacancy, \( V_{Ga} \). The latter, if isolated, would have a charge \( Z_A = 3 \), but if complexed with Si, \( Z_A \) could be 2, or even 1. As shown earlier, we can then calculate \( N_D \) and \( N_A \) from \( N_{ii,eff} \). Under the
assumptions, $Z_\| = 1$ and $Z_\perp = 1$, 2, or 3, the results are: $N_{\|} = 3.57, 2.77, \text{or } 2.37 \times 10^{18} \text{ cm}^{-3};$ and $N_\perp = 2.40, 0.80,$ or $0.40 \times 10^{18} \text{ cm}^{-3},$ respectively. To decide among these three possibilities it would be helpful to determine [Si] from another source, such as secondary ion mass spectroscopy, and $[\text{V}_{\text{Ga}}]$ from positron annihilation or electron paramagnetic resonance.

In summary, we have used the quantum-based magnetoeconductivity $\Delta \sigma$ vs $T$ to develop a function $T_{\text{po}}(T)$ that quantitatively explains not only $\Delta \sigma$ vs $T$ but also $\Delta \sigma$ vs $B$ and $\mu_B$ vs $T$ in degenerate $\beta$-Ga$_2$O$_3$. We also showed that the behavior of $\sigma$, $\Delta \sigma$, and $\mu_B$ in $\beta$-Ga$_2$O$_3$ is much different than that in ScN, a simpler system for which a constant $T_{\text{po}}$ well explains both $\Delta \sigma$ vs $T$ and $\mu_B$ vs $T$. The methodology used to develop the function $T_{\text{po}}(T)$ is directly applicable to other complex semiconductors.

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Author Contributions
D.C.L. and K.D.L. designed and directed this study. D.C.L. carried out the electrical, optical, and theoretical analysis. K.D.L. developed the degenerate, homoepitaxial layer growth. Both authors contributed to writing the manuscript.

Additional Information
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