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# Determination of the Electron Masses in Stannic Oxide by Submillimeter Cyclotron Resonance

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Submillimeter measurements of the effective masses yield values of $m_\perp^* = 0.299m_0$ and $m_\parallel^* = 0.234m_0$ for the electron. The density-of-states effective mass is $0.275m_0$. These direct measurements resolve the long-standing conflict among a variety of reports which have ranged from 0.1 to $0.4m_0$.

## I. INTRODUCTION

We have measured for the first time the electron cyclotron resonance effective-mass tensor[1] for stannic oxide $SnO_2$, using high-quality high-mobility stannic oxide crystals[2] and a submillimeter gas laser spectrometer.[3] This is the first direct effective-mass measurement ever made on this wide-band-gap semiconductor. A survey of the published estimates of the electron effective mass, made largely from transport and infrared experiments, shows that an accurate measurement has been sorely needed. Published effective-mass values[4-8] range from $0.1m_0$ to over $0.4m_0$. No information has been available on the anisotropy of the effective mass. We find $m_\perp^* = 0.299m_0$ and $m_\parallel^* = 0.234m_0$ and a density-of-states effective mass of $0.275m_0$.

Determinations of the effective mass $m^*$ from analyses of Hall measurements of carrier concentration as a function of temperature gave the highest values, $0.39m_0$ in one instance,[2] and $(0.41 \pm 0.1)m_0$ in another.[4] On the other hand, Marley and Dockerty[5] obtained only $0.22m_0$ from a similar analysis. These same authors also report a value of $0.12m_0 < m^* < 0.18m_0$ from thermoelectric power considerations. This latter range is similar to Morgan and Wright's[6] result of $0.1m_0 < m^* < 0.17m_0$, also from thermoelectric measurements, but they themselves point out that the accuracy of this method for determining $m^*$ is poor. Nagasawa,[4] in contrast, found $m^* = 0.33m_0$ from similar thermoelectric measurements. Summitt and Borelli[7] mention an $m^*$ from a measurement of Faraday rotation of $0.2m_0$. Finally, Crabtree, Mehdi, and Wright[8] report a value of $m^* = 0.17m_0$ determined from infrared absorption measurements. Such a variation in the reported conclusions on $m^*$ is not surprising, particularly when one considers the variation in the quality of stannic oxide crystals available for most of these studies. The important thing to note is that all of these measurement techniques require a knowledge of the carrier concentration and scattering mechanisms for their analyses. As such, they are easily subject to large uncertainties.

Cyclotron resonance using submillimeter-wavelength laser spectrometers has recently been developed as a powerful technique for determining the carrier effective masses in low-mobility materials, that is, materials in which the mobility is so low that the condition for observing cyclotron resonance, $\omega_c\tau \geq 1$, is not satisfied at the microwave frequencies of conventional cyclotron resonance measurements. The submillimeter measurements have already proven very useful in the study of CdS,[9] CdTe,[10] CdSe,[11] and ZnO, which have mobilities in the range 100–500 $cm^2\,V^{-1}\,sec^{-1}$.

Stannic oxide has heretofore occupied this category of low-mobility materials so that electron cyclotron resonance could never before be attempted. Recently, however, high-quality high-mobility stannic oxide single crystals became available,[2] assuring the success of an accurate cyclotron resonance measurement of the effective-mass tensor.

These crystals have a liquid-nitrogen Hall mobility of about 9000 $cm^2V^{-1}sec^{-1}$, which is nearly an order of magnitude higher than has previously been available. Indeed, the peak mobilities at lower temperatures now exceed 13000 $cm^2V^{-1}sec^{-1}$. We have therefore combined the submillimeter technique with the use of these new crystals to make direct cyclotron resonance measurements of the electron

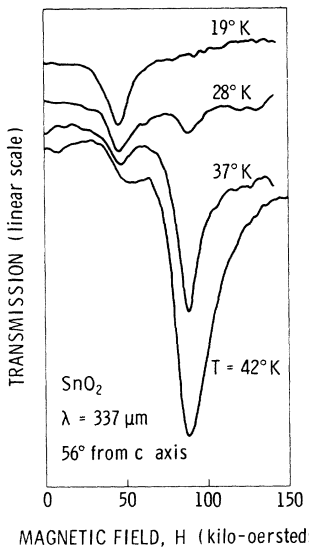


FIG. 1. Transmission through $SnO_2$ at several temperatures vs magnetic field. An HCN laser provided continuous-wave monochromatic radiation at a wavelength of 337 $\mu$m. The high-field resonance is a true electron cyclotron resonance; the low-field absorption line has not been identified.

effective-mass tensor in stannic oxide. The tensor elements are $m_\perp^* = (0.299 \pm 0.002) m_0$ and $m_\parallel^* = (0.234 \pm 0.002) m_0$. This is the most direct and reliable measurement made so far.

## II. PROPERTIES OF STANNIC OXIDE SPECIMENS

Stannic oxide crystallizes in the rutile structure, a structure with tetragonal $D_{4h}$ symmetry, and the conduction-band minimum is thought to occur at the zone center.[12] The effective-mass tensor is thus diagonal and is described by the two masses $m_\perp$ and $m_\parallel$ referenced with respect to the $c$ axis. As a result, cyclotron resonance absorption measurements on samples which include two different angles between the $c$ axis and the magnetic field are sufficient to determine the two elements of the mass tensor. The specimens used in this study were single crystals grown by a chemical vapor deposition technique described elsewhere.[13] Two crystals were selected from a growth run in which the crystals have typically shown an $n$-type carrier concentration of $7\times10^{15}$ cm$^{-3}$ and a Hall mobility of 250 cm$^2$V$^{-1}$sec$^{-1}$ at 300 °K. At 77 °K the carrier concentration found is $2\times10^{15}$ cm$^{-3}$ and the Hall mobility is 9000 cm$^2$V$^{-1}$sec$^{-1}$. The two crystals were lapped and polished to provide flat and parallel faces at an angle with respect to the $c$ axis of 34° on one sample and 56° on the second. These angles were determined by, and made use of, a natural (011) twin plane in the crystals and, consequently, were accurately known. Laue x-ray patterns made from the finished mounted samples confirmed that the angle was accurate to within $\frac{1}{4}$°; the final alignment of the sample and the magnetic field during a measurement was well within $\frac{1}{2}$°.

## III. EXPERIMENTAL RESULTS

The submillimeter gas laser spectrometer system used has been described previously.[3] Our measurements were made at three wavelengths, 337, 220, and 195 $\mu$m, by using an HCN, $H_2O$, and DCN continuous-wave laser, respectively. A water-cooled copper solenoid provided a steady magnetic field parallel to the direction of propagation of the unpolarized monochromatic radiation. Figure 1 shows the essential features of the experimental observations; this example shows the transmission of 337-$\mu$m radiation through the 3-mm-thick specimen as a function of applied magnetic field intensity for several temperatures. These curves are tracings of strip chart recordings which were taken while the magnetic field intensity was swept linearly from zero to 150 kOe in 2.5 min.

At temperatures below 28 °K only the absorption line at lower field is seen; the identity of this line has not been established. As the temperature is increased, the second line at higher field appears and grows stronger. This absorption is a true cyclotron-resonance absorption which yields the effective mass according to the relation $m^* = eH/\omega_c$, where $H$ is the magnetic field intensity at resonance and $\omega_c$ is the measuring frequency. We find this mass to be independent of frequency and of temperature within the indicated ranges, showing that neither a plasma nor a polaron correction needs to be made. The absorption strength of this resonance increases with temperature because electrons are excited thermally into the conduction band from the shallow donor energy levels. Since our measurements are taken in the quantum limit, where the distance between the Landau levels is larger than the average thermal energy $kT$, the absorption constant, at the resonance $\alpha_r \equiv -\ln(I_r/I_0)$, where $I_r$ and $I_0$ are the transmitted intensities on and off resonance, respectively, should show approximately the same temperature dependence as the carrier concentration. Consequently, this cyclotron resonance absorption constant was calculated and compared to the carrier concentration as a function of temperature obtained from Hall-effect measurements on a comparable sample. The result is shown in Fig. 2. It is seen that the slope of the absorption constant and of the carrier concentration are in good agreement within the limit of error, conservatively ±10%, thus supporting the identification.

Returning now to the absorption line seen on the low-field side of the electron cyclotron resonance line, this particular absorption cannot be associated with an effective-mass-type cyclotron resonance

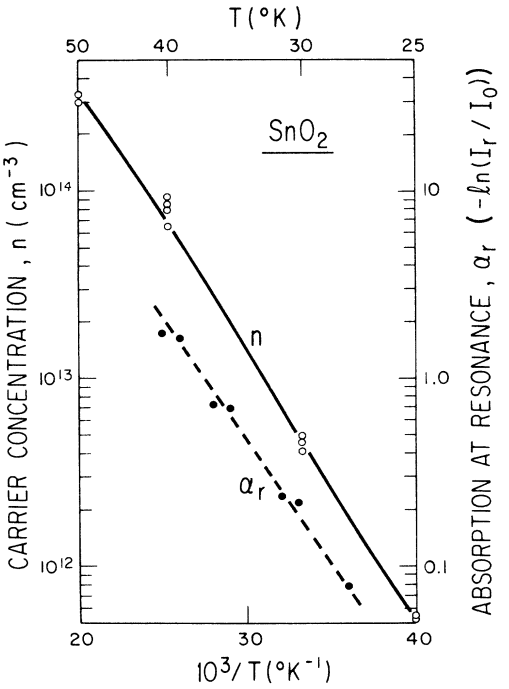


FIG. 2. Comparison of the temperature variation of the absorption at resonance observed in the sample of Fig. 1 with the temperature variation of the carrier concentration determined from Hall-effect measurements made on a comparable sample. The good agreement in the slopes of the two curves confirms the identification of this resonance with electron cyclotron resonance.

nor a simple harmonic because it does not scale properly with frequency; that is, its "apparent" effective mass varies with the frequency of the radiation. For example, it is $0.108m_0$ at 195 $\mu$m and $0.138m_0$ at 337 $\mu$m. It also varies in strength from sample to sample. We have not identified the source of this absorption. Therefore, this line will be the subject of a separate investigation.

## IV. ANALYSIS OF RESULTS

The effective masses corresponding to the electron cyclotron resonances are $m^* = (0.287 \pm 0.001)m_0$ for $\angle(H, c) = 34°$ and $m^* = (0.274 \pm 0.001)m_0$ for $\angle(H, c) = 56°$. The observation of only one true cyclotron resonance peak shows that our assumption that the conduction band has only a single $k = 0$ minimum is valid. From these observed effective-mass values we can now calculate tensor components $m_\parallel$ and $m_\perp$ using the well-known formula[14]

$$[m^*(\theta)]^2 = m_\parallel m_\perp^2/(m_\parallel \cos^2\theta + m_\perp \sin^2\theta) ,$$

where $\theta$ is the angle between the $c$ axis and the magnetic field. The result of this calculation is $m_\perp = (0.299 + 0.002)m_0$ and $m_\parallel = (0.234 + 0.002)m_0$. The uncertainties include a $\pm\frac{1}{2}°$ uncertainty in the angle $\theta$.

Stannic oxide is a polar material with a polaron coupling constant rear unity.[2] Therefore, the mass values above must be regarded as low-frequency polaron effective masses rather than bare masses associated with a rigid lattice. Our laser frequencies are of the order of magnitude of $10^{12}$ Hz which is much smaller than the frequency of the nearest longitudinal optical phonon[15] at $8 \times 10^{13}$ Hz.

It has not been necessary to correct for plasma-shifted cyclotron resonance because $\omega_c \gg \omega_p$, where $\omega_p = Ne^2/m^*\epsilon$. According to Fig. 2, our free carrier concentration $N$ is always less than $10^{14}$ cm$^{-3}$ at the temperatures of our measurements. Therefore, the plasma frequencies $\omega_p$ for each measurement shown in Fig. 1 lie in the microwave range of the spectrum, whereas these laser frequencies lie in the submillimeter range. The correction would have to be made, however, if measurements were made at temperatures above 75 °K by using the relation $\omega_c = \omega[1 - \omega_p^2/\omega^2]^{1/2}$, where $\omega$ is the laser frequency. For example, at 75 °K, $N \approx 10^{15}$ cm$^{-3}$ because of thermal excitation of free carriers and the wavelength corresponding to the plasma frequency would be 2 mm. This would require a 1% correction in the cyclotron frequency.

The anisotropy ratio $m_\perp/m_\parallel$ is 1.28. We note that since $m_\perp > m_\parallel$, the conduction-band constant energy surfaces are prolate spheroids. The density-of-states effective mass for the conduction band, $m_{dc} = (m_\perp^2 m_\parallel)^{1/3}$, is $0.275m_0$. Finally, we can note that the existance of a single conduction-band minimum is a strong indication that stannic oxide is a direct-gap semiconductor; no indirect-gap semiconductor is known in which the valence-band maximum is at $k \neq 0$.

## V. CONCLUSION

Using the technique of submillimeter cyclotron resonance, and high-quality crystals of stannic oxide, we have made the first accurate measurement of the conduction-band effective-mass tensor in $SnO_2$. The tensor components found are $m_\perp = 0.299m_0$ and $m_\parallel = 0.234m_0$. The corresponding density-of-states effective mass is $0.275m_0$. An additional absorption line is observed at low temperatures which does not scale with frequency and it has not been identified.

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# Phonons, Polaritons, and Oblique Phonons in $LiIO_3$ by Raman Scattering and Infrared Reflection*

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A detailed Raman-scattering investigation of $LiIO_3$, combined with the polarized infrared-reflectivity measurements, is reported. The dielectric constants determined by the Lyddane-Sachs-Teller (LST) relation ($\epsilon_{xx}=6.7$, $\epsilon_{zz}=6.1$) do not reveal any large contribution by the lattice dynamics to the low-frequency dielectric response. The high-temperature study of the TO Raman modes (till 220 °C) does not show any mode "softening," which could explain the critical dielectric behavior observed at very low frequencies. The study of the $A$-symmetry polariton curves has reconfirmed the LST dielectric values. The angular dispersion of the two upper oblique phonons of the $A$ and $E_1$ symmetry is compared with theory. The intensity dependence of these oblique phonons enables the determination of the second-harmonic-generation coefficient $d_{13}$ and the linear electro-optic coefficient $r_{13}$ in $LiIO_3$. These values are compared with other published data.

## INTRODUCTION

There has been much interest lately in iodates as new nonlinear optic materials. Of this group $LiIO_3$ is of special interest since its nonlinear coefficients are comparable with the second harmonic nonlinear coefficient $d_{13}$ of $LiNbO_3$, and the second harmonic generation (SHG) is phase matchable.[1] Several investigations into the crystal properties of $LiIO_3$ have resulted in contrasting reports,[1–4] and as yet an unexplained dielectric behavior.[5]

The dielectric constant along the $z$ axis exhibits an unusual temperature and frequency behavior. As the temperature is increased from 21.5 to 256 °C (where presumably a destructive phase transition occurs), the $\epsilon_{zz}$ measured at 1000 Hz increases from 554 to values higher than 30 000, whereas the $\epsilon_{xx}=\epsilon_{yy}$ is almost temperature insensitive.[1] As a function of frequency at room temperature, $\epsilon_{zz}$ decreases from a value of 554 at 1000 Hz to approximately 6 at 3 MHz.[5] Pyroelectricity has been observed in $LiIO_3$; however, attempts to observe electric polarization switching with fields up to 6 kV/cm were unsuccessful.[1]

The following paper describes a detailed investigation of the Raman scattering at various temperatures combined with the polarized infrared reflectivity of $LiIO_3$. These studies provide information on the structural makeup of the crystal as determined from the selection rules. Also, the phonon contribution to the abnormal dielectric-constant behavior is determined from the generalized Lyddane-Sachs-Teller (LST) relation. As the lowest polariton dispersion curve also depends on the static dielectric constant, an effort was made to follow the polariton dispersion in $LiIO_3$ at room