Ordering and Absolute Energies of the $L_6{}^c$ and $X_6{}^c$ Conduction Band Minima in GaAs†

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Resolved critical point structures in Schottky-barrier electroreflectance spectra of Ga $3d^V$-sp^3 conduction band transitions in the 20–22-eV range provide a direct proof that the $L_6{}^C$ equivalent minima lie approximately 170 ± 30 meV *below* the $X_6{}^C$ minima in GaAs. This ordering, opposite to that assumed and apparently supported by previous experiments, is in fact consistent with these experiments and provides natural explanations for many formerly puzzling features of GaAs.

In 1960, Ehrenreich[1] reviewed the available experimental and theoretical evidence and proposed that the lowest $L_6{}^C$ local equivalent minima of the conduction band of GaAs were far enough in energy above the lowest $X_6{}^C$ local equivalent minima in this direct-gap material to be safely ignored in such phenomena as the Gunn effect that depend on the existence of higher indirect minima. Numerous later experiments apparently provided further confirmation of this hypothesis.[2] Yet problems remain: The activation threshold of 0.38 eV determined from recent high-temperature[3] and high-pressure[4] Hall-effect and resistivity data is significantly lower than the measured $\Gamma_6{}^C$-$X_6{}^C$ separation of 0.43–0.48 eV determined by intra-conduction-band absorption.[5,6] Also, the activation energy of N isoelectronic traps in the technologically important $GaAs_xP_{1-x}$ alloy series shows an anomalous increase in the binding energy as the As fraction increases.[7,8]

Here, we present the first direct measurement of the relative energies of the $\Gamma_6{}^C$, $L_6{}^C$, and $X_6{}^C$ conduction-band minima in GaAs. Our synchrotron-radiation Schottky-barrier electroreflectance (ER) spectra of the Ga $3d^V$-sp^3 core-conduction band transitions in the 20–22-eV range show that the $L_6{}^C$ minima actually lie 170 ± 30 meV *below* the $X_6{}^C$ minima in GaAs. We find that transport[3,4] and photoemission[9,10] data that apparently supported the opposite ordering can be reinterpreted to be *entirely consistent* with the $L_6{}^C$ minima below the $X_6{}^C$. The new ordering also provides a natural qualitative explanation for the behavior of the binding energy of the N isoelectronic trap, further suggesting that the L-symmetry components in the wave functions of the trapped electrons will be important for luminescence-efficiency calculations;[11] moreover, it shows that the photoemission studies[10] of transport properties nominally at the $X_6{}^C$ minima have actually been at the $L_6{}^C$, which also implies that the current descriptions of the operation of GaAs Gunn oscillators[12] will have to be re-examined.

Schottky-barrier ER measurements were performed at the Synchrotron Radiation Center of the Physical Sciences Laboratory of the University of Wisconsin on n-type GaAs single crystals of $\langle 110\rangle$ and $\langle 111\rangle$ orientations with impurity concentrations of 1.5×10^{17} cm^{-3} Si and 4.0×10^{17} cm^{-3} Te, respectively. Details of the Schottky barrier[13] and uv optical[14] techniques are given elsewhere. These measurements differed from our previous work on GaAs[15] because we used an angle of incidence, $\varphi = 60°$, that optimized[16] the signal-to-noise ratio and allowed the Γ-L-X fine structure to be resolved.

ER spectra for the relatively lightly and heavily doped crystals are shown at the top and bottom of Fig. 1, respectively. The dominant features, at 20.49 and 20.92 eV, are structures arising from critical points between the Ga $3d_{5/2}{}^V$ and Ga $3d_{3/2}{}^V$ core levels and the $X_6{}^C$ local minima of the sp^3 conduction band. This assignment follows directly from the line shape and relative-amplitude comparisons with GaP,[15-17] where the $X_6{}^C$ minima are the absolute conduction-band minima and the origin of the structure is unambiguous. It is further supported by the exciton binding energies of Ga $3d^V$-$X_6{}^C$ transitions, which are of the order of 100 meV for GaP[15,17,18] and GaSb[18,19] —and, with this new assignment, for GaAs also.[19]

The "anomalous" features in Fig. 1 are the small spin-orbit-split structures near 20.32 and 20.76 eV, and the structure near 20 eV that appears only in the heavily doped sample. The only possible Ga $3d^V$-sp^3 conduction-band critical points

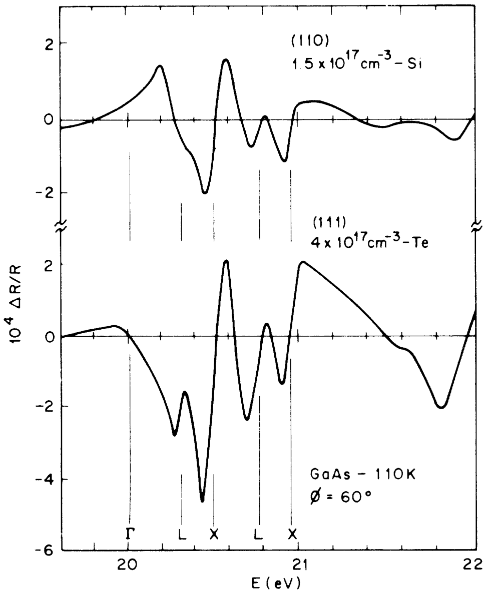

FIG. 1. Schottky-barrier electroreflectance spectra from Ga $3d^V$ core levels to the lower sp^3 conduction band for relatively lightly (top) and heavily (bottom) doped single crystals of GaAs.

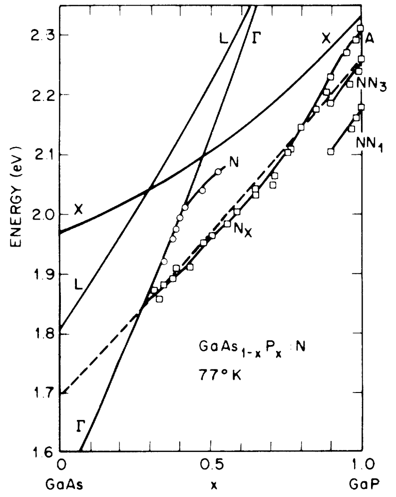

FIG. 2. Variation of the $\Gamma_6{}^C$, $X_6{}^C$, and isoelectronic N trap energies in $GaAs_{1-x}P_x$ alloys from Ref. 8, and of the $L_6{}^C$ from Schottky-barrier electroreflectance data for GaAs and GaP (this work). The variation (dashed line) of the N trap energy calculated from Eq. (1) is also shown.

in the 20–22 eV spectral range are those associated with the $\Gamma_6{}^C$, $L_6{}^C$, and $X_6{}^C$ minima since the Ga $3d^V$ bands are flat to within 0.1 meV.[20] Since the $\Gamma_6{}^C$-$X_6{}^C$ separation at 2 K is 0.462 eV,[6,21] the 20 eV feature in the lower spectrum clearly arises from the Ga $3d_{5/2}{}^V$-$\Gamma_6{}^C$ critical point near 20.02 eV. It appears only in the spectrum of the heavily doped sample, presumably because the selection rules are relaxed by the impurity fields in this material. The remaining structures 170 ± 30 meV below Ga $3d^V$-$X_6{}^C$ are therefore the Ga $3d^V$-$L_6{}^C$ critical points. Chelikowsky has recently calculated[22] the matrix elements for the Ga $3d^V$-sp^3 conduction-band points at $\Gamma_6{}^C$, $L_6{}^C$, $X_6{}^C$, and $X_7{}^C$. He found that the matrix element connecting the $L_6{}^C$ is finite but smaller than that connecting the $X_6{}^C$, in agreement with our results.

But numerous experiments have apparently shown that the $L_6{}^C$ minima are well above the $X_6{}^C$. However, without exception, these results can be reinterpreted to be consistent with the $\Gamma_6{}^C$-$L_6{}^C$-$X_6{}^C$ ordering found here. We briefly consider two major types of data concerning the transport properties (as a function of pressure and temperature) and photoemission; and we shall present a more extended analysis elsewhere.

The apparent activation energy of 0.38 determined in careful high-temperature transport measurements[3] actually falls about 0.1 eV above the true indirect threshold, because at the reference (500 K) temperature, a nonnegligible fraction of electrons have already transferred to $L_6{}^C$ and $X_6{}^C$. Thus the activation energy, determined from a semilogarithmic plot of the 600–700 K data, appears larger than the true value. The high-pressure resistivity and Hall-coefficient data,[4] previously explained by a $\Gamma_6{}^C$-$X_6{}^C$ model, also can be fitted very well with the $\Gamma_6{}^C$-$L_6{}^C$-$X_6{}^C$ model, provided that the mobility of electrons in the $L_6{}^C$ minima is about 10% that of the electrons in $\Gamma_6{}^C$. This is consistent with transferred-electron measurements (since GaAs Gunn oscillators work) and also with the hydrostatic pressure measurements on GaSb,[23] which show a $\Gamma_6{}^C/L_6{}^C$ mobility ratio of 7.5 at room temperature. Photoemission measurements[9,10] show structures at 1.42, 1.72, 1.81, and 2.2 eV at room temperature, which is consistent with our interpretation if the 1.72- and 1.81-eV structures are simply reassigned to $L_6{}^C$ and $X_6{}^C$, respectively. Since the density of states is similar for both, this reassignment presents no essential difficulties.

The $\Gamma_6{}^C$-$L_6{}^C$-$X_6{}^C$ ordering provides a natural qualitative explanation of the unusual increase of the binding energy of the N isoelectronic trap in $GaAs_{1-x}P_x$ alloys with increasing As fraction, as seen in Fig. 2. Here, data[8] are shown for the variation of the $\Gamma_6{}^C$ and $X_6{}^C$ threshold and N trap energies as a function of x. Also shown are our variation of the $L_6{}^C$ threshold energy, using our

$L_6{}^c$ values for GaAs and GaP and assuming a reasonable bowing parameter (90% that of $\Gamma_6{}^c$) for $L_6{}^c$. To calculate the N energy E_N, we make use of the large (approximately equal) densities of states of $L_6{}^c$ and $X_6{}^c$ relative to that of $\Gamma_6{}^c$ and the relatively small dispersion of these minima with $\vec{k}$ to represent the conduction band in a two-level model with energies $E_L(x)$ and $E_X(x)$, where x is the P fraction of the alloy. Taking a Koster-Slater representation[24] for the dominant, short-range part of the isoelectronic trap potential[25] and considering only the off-diagonal coupling, the two-band Hamiltonian becomes

$$\det\begin{vmatrix} E_L(x)-E_N & V \\ V & E_X(x)-E_N \end{vmatrix}=0, \qquad (1)$$

where E_N is the trap energy and V is the Koster-Slater interaction strength. The form of Eq. (1) is such that the trap energy reaches its maximum, $-V$, when $E_L=E_X$. From this, we determine $V=0.18$ eV and calculate E_N according to Eq. (1). The model is oversimplified because it does not include the effect of increasing strain around the N site with an increasing As concentration, which also acts to increase V.[26] Nevertheless, the results, shown in Fig. 2, are in remarkable agreement with the experiment and provide direct evidence of the *combined* L and X nature of the wave functions of the isoelectronic trap. Thus any complete description of the properties of this trap must include the effects of $L_6{}^c$.

Other direct results of the $\Gamma_6{}^c$-$L_6{}^c$-$X_6{}^c$ reordering include the following: First, the energy discrepancies between the transport,[3,4] optical,[5,6] and photoemission[9,10] data are now completely resolved. Second, the results are in excellent agreement with the predictions of recent nonlocal-pseudopotential calculations [$X_6{}^c - L_6{}^c = 150$ meV (Pandey and Phillips), 210 meV (Chelikowsky and Cohen)][27] for GaAs, probably because the cores of these elements are isoelectronic. Third, Gunn-diode operation and the analysis of transport properties by photoemission in GaAs are found to involve the $L_6{}^c$ minima and not the $X_6{}^c$. These results should allow the development of theories to describe quantitatively various properties of deep traps and the principle of operation in devices involving GaAs and related materials.

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Optical and Electrical Properties of Graphite Intercalated with HNO_3 †

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Drude edges are observed in reflectance spectra and compared with the dc transport measurements in the lamellar compounds $C_{6n}HNO_3$ with $n=1$, 2, and 3. Both measurements confirm the general metallic character of these materials, but the optical data are inconsistent with a simple Drude model. We suggest that this is due either to a complex background dielectric constant or to a multiple-carrier Fermi surface.

Graphite intercalation compounds consist of one or more planes of hexagonally arrayed carbon atoms separated by monolayers of intercalated atoms or molecules.[1] The number of contiguous carbon planes is referred to as the stage of the compound. Many donors (e.g., alkali metals) and acceptors (halogens and acid radicals) have been successfully intercalated. A universal feature of all these compounds is a large increase in the a-axis electrical conductivity, presumably due to an increase in the free carrier density which accompanies the transfer of charge between the graphite and intercalant layers.[2] In this Letter we report the first systematic study of variations in Drude-like reflectance with the intercalant concentration. The optical results confirm the metallic character of these compounds, but a comparison with the dc transport measurements shows that these are not simple Drude metals. Our results are similar to the "transmission windows" reported by Hennig,[3] which could not be analyzed quantitatively because the thickness of the cleaved specimens was unknown.

This Letter deals specifically with the first three stages of the graphite-HNO_3 lamellar compounds. The starting material was highly oriented pyrolytic graphite,[4] in which the spread in c axes of individual crystallites is of order 1 and the crystallite size is of order 1μm. Individual samples for the optical and transport experiments were intercalated using methods developed by Fuzellier.[5] These consist of employing distilled HNO_3 instead of red fuming HNO_3 which allows one to obtain concentrations up to stage 1 without further adjustment of chemistry. The samples were characterized by x-ray, weight-uptake, c-axis dilation, and chemical analyses.[6] The results are all consistent with the chemical formula $C_{6n}HNO_3$, where n denotes the stage of the compound, as previously determined by Ubbelohde.[7] The c axis repeat distance I_c follows the relation $I_c = 7.8 + 3.35(n-1)$ Å, also in agreement with previous reports.[5,7]

Figure 1 shows the reflectance spectra of freshly cleaved c surfaces for the first three stages. Unpolarized light at near-normal incidence was used (i.e., with the polarization perpendicular to $\vec{c}$). The stage 2 and 3 compounds were measured at room temperature in a flow of N_2 gas, while the stage 1 compound was immersed in carbon tetrachloride at -20°C since it is unstable at higher temperatures.[5] The samples were x-

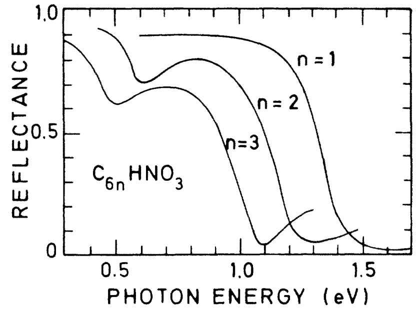

FIG. 1. Reflectance spectra of stage 1, 2, and 3 graphite nitrate intercalation compounds.