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# Experimental Evidence for a Negative-$U$ Center in Gallium Arsenide Related to Oxygen

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Fourier-transform infrared spectroscopy on the charge-state-dependent local modes of the off-center substitutional oxygen impurity in GaAs has revealed an inverted ordering of the two gap levels. The metastable one-electron state shows the characteristic disproportionation into the zero- and the two-electron states. From the thermally activated decay of the local mode lines and the observed threshold energies for the photoionization cross sections $\sigma_p^0(1)$ and $\sigma_n^0(2)$, binding energies of 0.15 and 0.62 eV for the first and the second electron, respectively, are deduced.

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The role of oxygen in GaAs has very recently attracted renewed interest. Whereas the old work on oxygen in GaAs was focused on the interrelation with the semi-insulatating (SI) behavior of this material—with a negative result[1]—new activities were excited by the observation of two local modes at 715 and 731 $\mathrm{cm}^{-1}$.[2] These modes, showing a characteristic Ga isotope fine structure, were attributed to oxygen bonding with two gallium atoms (Ga-O-Ga defect).[3] The incorporation of oxygen as the major constituent of this defect is now beyond any doubt due to the observation of the $^{16}$O/$^{18}$O isotope shift in $^{18}$O-doped samples.[4] It has been suggested that this defect is the analog of the $A$ center in silicon (see Fig. 1).[3,4] However, in contrast to Si, where this defect is created only by high-energy electron irradiation,[5] in GaAs it is frequently found in as-grown material. The most fascinating property of these local modes is their photosensitivity. In SI GaAs, where the Fermi level is located near midgap, a conversion of the band at 731 $\mathrm{cm}^{-1}$, $A$, into the band at 715 $\mathrm{cm}^{-1}$, $B$, is observed during illumination with below-bandgap light ($h\nu \geq 0.8$ eV). Also, the reverse process occurs under certain circumstances.

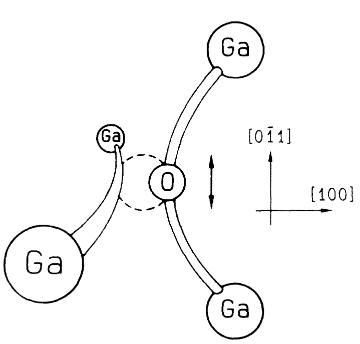


FIG. 1. Structural model of the Ga-O-Ga defect. Bonding preferentially with two Ga atoms, the oxygen atom moves off center in the [100] direction. The $A$ center in silicon is obtained when the Ga atoms are replaced by Si atoms.

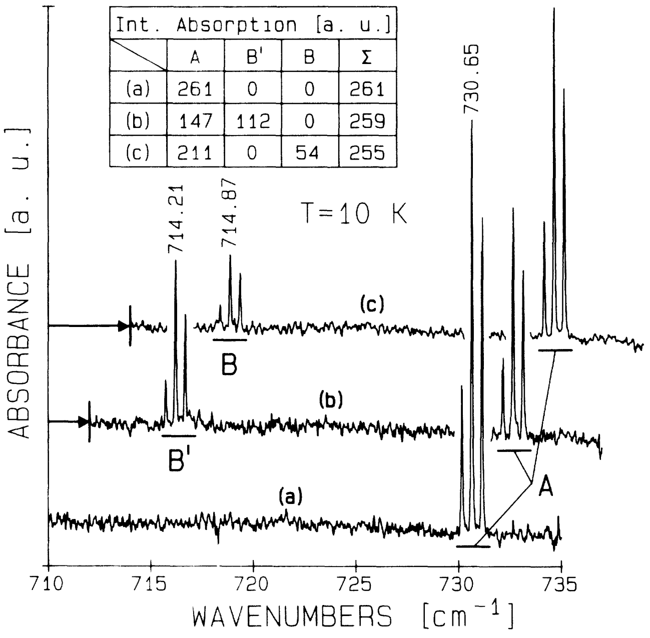
Essential for the discussion in this Letter is the assignment of bands $A$ and $B$ to two different charge states of the defect.[6] Experimentally it is found that after cooling a SI sample in the dark only band $A$ appears. The conversion rate from $A$ to $B$ is proportional to the photoionization cross section $\sigma_n^0$ of the omnipresent deep donor $EL2$. It is concluded that the conversion is caused by a charge-transfer process from the partially occupied $EL2$ level to the unoccupied oxygen defect via the conduction band. It should be mentioned that a charge-state-induced shift of the local mode frequency has also been reported for the $A$ center in Si.[7]

More detailed studies revealed that a third band $B'$ exists, shifted from $B$ by 0.66 $\mathrm{cm}^{-1}$ to lower energy.[8] This band emerges during the optically induced conversion from $A$ to $B$ at an intermediate stage. The kinetics is quantitatively described by a model considering successive capture of conduction-band electrons, which have been photoexcited from the $EL2$ level. The corresponding depopulation of the $EL2$ level ($EL2^0 \rightarrow EL2^+$) has been observed experimentally. Thus, there is conclusive experimental evidence that the band $B'$ corresponds to a third charge state, where $A$, $B'$, and $B$ now must be assigned to the zero-, one-, and two-electron states, respectively. From a comparison of samples with different positions of the Fermi potential, it was concluded that the corresponding two energy levels are located in the upper half of the bandgap. Remarkably enough, only the states with zero or two electrons (bands $A$ and $B$) are detected at thermal equilibrium. This observation led to the speculation that a new negative-$U$ center has been found, that is, a system where the second electron is bound more strongly than the first. The very unusual properties of negative-$U$ defects have first been elaborated for the vacancy in Si.[9]

In this work we present the experimental proof for this speculation and report the binding energies. Off-center substitutional oxygen in GaAs thus represents one of the few negative-$U$ systems in compound semiconductors known so far—there is evidence that also the $M$ center in InP and the *DX* centers in AlGaAs have negative-*U* characteristics[10,11]—and the first well-established example for such a defect in GaAs. It should be noted that all major experimental results have been obtained by Fourier-transform infrared spectroscopy on the local modes of this defect.

The samples investigated come from a not deliberately oxygen-doped SI GaAs crystal grown after the liquid-encapsulated Czochralski technique using a pyrolitic boron-nitride crucible and boric-oxide encapsulation. Thus oxygen in this material is a residual impurity. The concentration of the Ga-O-Ga defect is $\sim 1.1\times10^{15}$ cm$^{-3}$, as estimated from the strength of the local modes.[6] The carbon acceptor concentration is $2\times10^{15}$ cm$^{-3}$ and the *EL*2 concentration $\sim 1.1\times10^{16}$ cm$^{-3}$. At thermal equilibrium the Fermi level is pinned by the deep donor *EL*2 at about $E_C - 0.65$ eV thus providing the SI property with a room-temperature resistivity of $8\times10^{7}$ Ω cm and an activation energy of 0.76 eV for the free electrons. Infrared-absorption measurements were performed with a Fourier-transform spectrometer in the temperature range between 10 and 200 K. The sample size was $10\times10\times5$ mm$^3$.

A fingerprint for a negative-*U* system is the so-called disproportionation.[9] This means the thermodynamically driven spontaneous decay of the metastable electron state—prepared under nonequilibrium conditions—into the states with the next higher and the next lower number of electrons. In Fig. 2 a sequence of absorption spectra is shown illustrating disproportionation in the case of the Ga-O-Ga center. After cooling the sample from room temperature to 10 K in the dark, an absorption spectrum exhibiting only band *A* (zero-electron state) is observed. By a short illumination with photons of $0.8 \le h\nu \le 1.5$ eV, part of band *A* is converted into band *B'*. This conversion is caused by the capture of conduction-band electrons which have been photoexcited from the occupied *EL*2 center. Keeping the sample at 10 K, this state is stable for hours. Now, the sample is warmed in the dark to 95 K, kept at this temperature for 60 min, and then cooled to 10 K again. During this cycle band *B'* vanishes completely, band *A* increases, and, as a new feature, band *B* appears. The interpretation is as follows: By warming the sample to 95 K the one-electron state (band *B'*) is depopulated by thermal emission. The electrons emitted to the conduction band are captured by still occupied *B'* centers creating the two-electron state (band *B*). Recapture by ionized *EL*2 centers seems to be unimportant, evidently because of the small capture cross section at $T = 95$ K.[12] As a net effect any two *B'* centers must form one *B* center. Indeed, this is found from the integrated absorption strength (see inset of Fig. 2) where band *B'* decays exactly half into *B* and half into *A*.



| Int. Absorption [a. u.] | A | B' | B | Σ |
|---|---|---|---|---|
| (a) | 261 | 0 | 0 | 261 |
| (b) | 147 | 112 | 0 | 259 |
| (c) | 211 | 0 | 54 | 255 |

FIG. 2. High-resolution infrared-absorption spectra of SI GaAs containing the Ga-O-Ga defect: (a) after cooling the sample to 10 K in the dark, (b) after short illumination with 1.37-eV photons, and (c) after warming to 95 K and cooling to 10 K again. Inset: The integrated absorption (in arbitrary units) of bands *A*, *B'*, *B*, and all the three bands together (Σ) at each stage.

Next, the activation energy of the thermally induced decay of *B'* was determined. Two experimental sequences are possible. The simplest way is to warm the sample from a situation as in Fig. 2(b) and to observe the thermal decay of *B'*. However, the resulting transient is strongly nonexponential because there is no efficient recombination channel for the electrons being emitted to the conduction band. Recapture occurs in competition between unoccupied centers (*A*), singly occupied centers (*B'*), and ionized *EL*2 centers. It is better to transform first *EL*2 into its metastable state by illuminating the sample with photons of $1.0 \le h\nu \le 1.3$ eV.[1] Using this procedure, the optical interaction with *EL*2 is eliminated and band *B'* can be prepared by illuminating the sample with 1.45-eV photons. What occurs is the population of the one-electron state by direct photoexcitation of electrons from the valence band (see below). Now, an efficient recombination channel has been opened for thermally emitted electrons in the form of the direct recombination with acceptor-bound holes. The rate equation for the one-electron state (band *B'*) takes the form

$$\frac{d}{dt}N_1 = -e_1N_1\left(1-\frac{c_0nN_0}{e_1N_1}+\frac{c_1nN_1}{e_1N_1}\right),$$

where $N_0$, $N_1$, and $n$ are the densities of the zero-electron state, the one-electron state, and the free electrons, respectively, and $e_1$, $c_0$, and $c_1$ are the emission

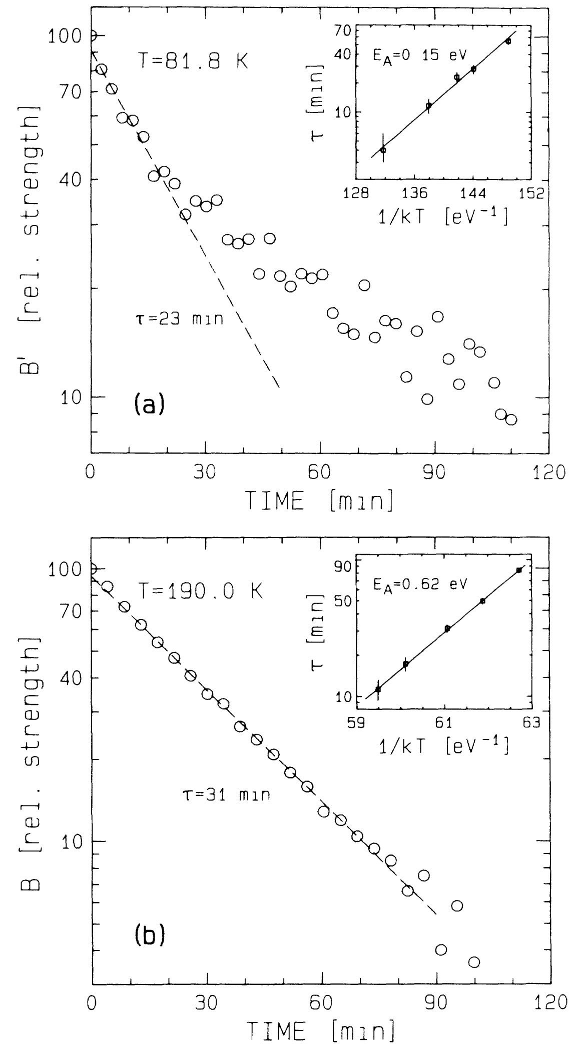


FIG. 3. Typical thermal decay of (a) band $B'$ (after bleaching the $EL2$ center) and (b) band $B$. Insets: An Arrhenius plot of the time constant.

rate and the capture coefficients, respectively. In Fig. 3(a) the experimental result at 82 K is shown. As expected from the rate equation, the transient is exponential in the beginning of the decay ($N_0 \ll N_1$) and nonexponential for decreasing $N_1$ density. As a consequence, only the initial part of the transient is suited for extracting the time constant $\tau$. Measurements of this kind give a time constant with an activation energy of $0.15 \pm 0.02$ eV.

Longer illumination at $T < 70$ K in the spectral region $0.8 \leq h\nu \leq 1.5$ eV leads to a complete conversion $A \rightarrow B$. This state is stable for temperatures up to $\sim 180$ K. At higher temperatures the decay of $B$ starts, accompanied by the reappearance of band $A$. In Fig. 3(b) the result at 190 K is shown. It is evident that the transient is purely exponential over the whole measurable range of more than an order of magnitude. The following process occurs: The second electron is thermally emitted to the conduction band, followed immediately by the first due to the smaller binding energy. Recapture can occur only at the unoccupied $EL2$ level. In other words, this is the thermally activated back reaction of the optically induced conversion $A \rightarrow B$ at low temperatures. This has been proved experimentally by measuring the $EL2$ absorption band before and after the decay of $B$. It comes out that after the decay the $EL2^+$ absorption has decreased and the $EL2^0$ absorption has increased, just as it is required from the above process. From the Arrhenius plot of the time constant $\tau$ an activation energy of $0.62 \pm 0.03$ eV is found for the decay of the two-electron state.

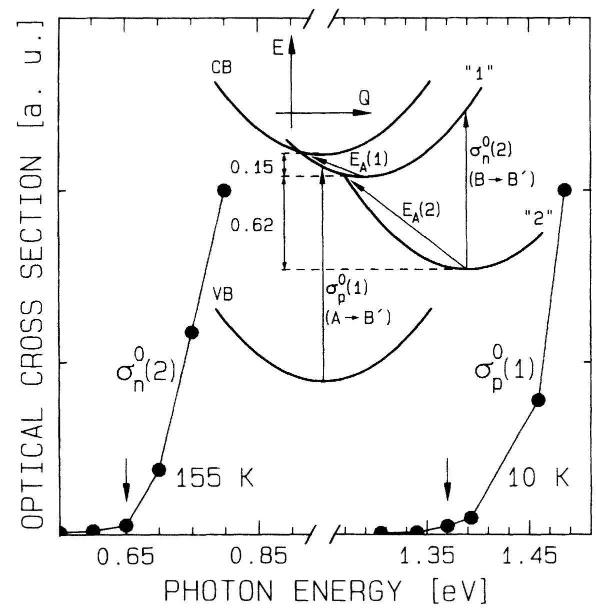


FIG. 4. Optical cross sections $\sigma_p^0(1)$ and $\sigma_n^0(2)$ near the threshold energies for the photoexcitation of (right) a valence-band electron to the zero-electron state and (left) an electron of the two-electron state to the conduction band. Inset: A tentative configuration-coordinate diagram. Thermal emission from the one-electron state ("1") and the two-electron state ("2") is denoted by $E_A(1)$ and $E_A(2)$, respectively. The low-energy thresholds of the observed optical transitions [$\sigma_p^0(1)$, $\sigma_n^0(2)$] are given by the energy difference of the corresponding curve minima (no-phonon process).

As a further independent experiment for the assignment of the gap levels, the photoexcitation properties of bands $A$, $B'$, and $B$ were investigated (see Fig. 4). First, in analogy to the decay of $B'$, the zero-electron state ($A$) was prepared by bleaching the $EL2$ center. Now, it is possible to transfer electrons directly from the valence band to the unoccupied oxygen center ($A \rightarrow B'$) by illuminating the sample with light of appropriate energy. A threshold energy of 1.37 eV is clearly observable for this process, described by the photoionization cross section $\sigma_p^0(1)$. Therefore, this completely independent measurement gives again a position of $\sim E_C - 0.15$ eV for the first level. For the optical determination of the second level, band $B$ was prepared by illuminating the sample at low temperatures with 1.37-eV photons. After that, the sample was warmed to 155 K. This temperature is high enough to inhibit bleaching of $EL2$ and, as shown above, low enough to avoid the thermal decay of $B$. Illumination with light now gives a threshold energy of 0.65 eV for the depopulation of $B$. The corresponding cross section is $\sigma_n^0(2)$, that is, the optical excitation of an electron to the conduction band. Hence, this experiment also gives a position of 0.60–0.65 eV below $E_C$ for the second level (at 155 K). Thus, the thermal decay of the local mode lines $B'$ and $B$ and the photoionization experiments confirm conclusively the negative-$U$ property of the Ga-O-Ga center. It follows that the second electron is bound more strongly than the first by 0.47 eV.

In some samples where—at equilibrium—both bands $A$ and $B$ are observed, temperature-dependent Hall-effect measurements give an activation energy of 0.43 eV for the free electrons.[6] If the Fermi level is pinned by a negative-$U$ center, the activation energy found experimentally should be half the binding energy of both electrons,[13] in our case $(0.15+0.62)/2 \sim 0.4$ eV. Thus, the previous Hall data are consistent with the level positions presented in this work and, furthermore, provide additional support for the negative-$U$ characteristic. The remaining difference is within the margins given by the experimental errors and the unknown temperature dependence of the level positions.

What is the driving force for the negative-$U$ behavior in this system? The $A$ center in Si can trap an additional electron with the associated acceptor level at $E_C - 0.17$ eV.[5] In comparison to Si the corresponding center in GaAs possesses one valence electron less to fill the bonds, so from this point of view binding of two electrons is not unexpected. In this case the charge states of the defect are 0, $1^-$, and $2^-$. The first electron is certainly localized in part on the Ga-O bonds since the local mode frequency is shifted considerably ($\sim 16$ cm$^{-1}$). From the direction of the shift a stronger ionicity of the bond, i.e., a preferred localization near the Ga atoms, may be deduced.[14] The second electron has only a minor influence on the local mode frequency and is, therefore, localized on the two other Ga atoms not bonding with the oxygen atom. It is this second electron which corresponds to the acceptor electron of the $A$ center in Si. As the origin for the negative correlation energy a lattice distortion induced by the first electron is suggested. From the similar fine-structure splitting of bands $A$, $B'$, and $B$ it is inferred that the geometry of the vibrating "molecule" Ga-O-Ga remains essentially unchanged in all charge states. Therefore, the lattice distortion must occur in the other part of the defect, the Ga atoms bonding with each other. This part of the defect is not accessible to local mode spectroscopy, so that other experimental techniques like spin-resonance measurments are required in order to shed light on details of the lattice distortion.

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*Note added.*—During the reviewing process of the present manuscript a Letter on the same subject was published by Skowronski, Neild, and Kremer.[15] Their thermal decay results and the conclusions drawn are similar to ours.

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