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New Evidence for the Two-Electron O^- State in GaP

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Optically detected magnetic resonance in oxygen-doped GaP shows that the infrared emission at 0.84 eV and its phonon replicas are due to a spin-triplet to -singlet transition of the *two*-electron state of oxygen. The resonance data also show that the two-electron center has axial symmetry along the [110] axis, indicating that after capturing the second electron a strong lattice relaxation takes place.

The role of oxygen in GaP has been studied extensively for many years by various techniques,[1] but the nature of the two-electron oxygen-related electronic states is still a matter of controversy. Experiments have shown that oxygen is a deep donor on a P site and that the neutral donor binds an electron by 0.895 eV at 1.6 K. Dean and Henry[2] have shown that in addition to the donor-acceptor transitions involving the deep oxygen donor, another infrared luminescence emission is also due to oxygen. A zero-phonon line at 0.84 eV accompanied by phonon replicas has been shown to shift upon replacing ^{16}O by ^{18}O. The luminescence was thought to result from a radiative transition of an electron from the excited 1*s* *E* state of the isolated oxygen donor to the 1*s* *A* ground state. In 1973, by using photocapacitance measurements, Kukimoto, Henry, and Merritt[3] and Henry[4] discovered that the deep O donor in GaP could bind two electrons to become O^-. After binding the first electron, the donor could capture a second electron with a subsequent large lattice displacement indicating that a substantial change in the O^- host bonds had taken place. Grimmeiss *et al.*[5] and Morgan,[6] on the other hand, interpreted their two-electron photocapacitance data by supposing that the selection rules were such that optical transitions between the X_1 conduction-band edge and the two-electron ground state were very weak and this could explain the observed high optical threshold energies without involving a large Franck-Condon shift. Recently, Morgan[7] reinterpreted the infrared spectra of Dean and Henry,[2] suggesting that the 0.8-eV emission involved radiative transitions of the second electron bound to oxygen. His conclusions were based on the differences between the phonon modes involved in the infrared spectra and those involved in the neutral-oxygen donor-to-acceptor pair luminescence.

We have studied the electron states in oxygen-doped GaP by the optically detected paramagnetic resonance (ODMR) technique. Our results show that the emitting level of the 0.84-eV transition, observed first by Dean and Henry,[2] is a spin triplet. The orientation dependence of the ODMR spectra and the observed strong hyperfine interaction with *one* Ga nucleus show that the symmetry of the center is lower than tetrahedral. These results can be explained if we suppose that the infrared band is a triplet-to-singlet transition of the two-electron O^- state, in agreement with Morgan,[7] and that after capturing the second electron lattice relaxation oc-

curs, leading to a substantial change in the O^- to host bonds, as suggested by Henry *et al.*[4]

The ODMR technique has been used successfully in recent years to investigate both high-purity and doped semiconductors.[8] In the ODMR experiment, one measures changes of the photoluminescence intensity induced by microwaves as the magnetic field is swept through resonance. Our apparatus has been described in detail elsewhere (see Cavenett[9]). The emissions at 2 K in various spectral regions were monitored in a direction parallel to the magnetic field with either a cooled PbS cell or a photomultiplier so that the microwave-induced changes in either the total intensity or in one of the circularly polarized emission components could be detected. The microwaves at 9 or 16.5 GHz were switched at audiofrequencies and the resonances were detected using a lockin operating at the microwave chopping frequency.

The majority of the GaP crystals used in these investigations were epitaxial layers doped with oxygen, some of which were also doped with either Zn, or Te, or both. Other crystals were either solution grown or nominally pure LEC-grown (liquid-encapsulated Czochralski grown) crystals. The photoluminescence spectra of the crystals showed the characteristic neutral-oxygen–related donor-acceptor bands in the red and near-infrared part of the spectrum.[10] The structured infrared band consisting of the 0.84-eV no-phonon line and its phonon replicas is shown in Fig. 1 and was observed only in those samples where the shallow-donor and -acceptor concentration was below 10^{17} cm^{-3}.[2] In the following we shall refer to this band as the O^- band.

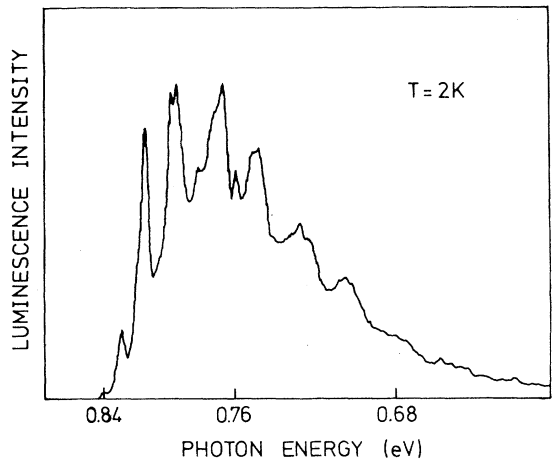

FIG. 1. Photoluminescence spectrum of the O^- band in oxygen-doped GaP.

By using the 799-nm line of the Kr laser we could preferentially excite the O^- band without exciting any of the other oxygen-related emission bands. A typical ODMR spectrum is shown in Fig. 2 for the magnetic field along the [110] direction and a microwave frequency of 16.5 GHz. Angular-dependence studies of the resonances at both microwave frequencies showed that these resonances can be accounted for by a spin triplet in the emitting state of the O^- center which has axial symmetry around the [110] direction and a nuclear hyperfine interaction with one Ga nucleus. The spin Hamiltonian for such a system is the following[11]:

$$\mathcal{H} = g_{\parallel}\mu_B B_z S_z + g_{\perp}\mu_B (B_x S_x + B_y S_y) + D[S_z - \tfrac{1}{3}S(S+1)] + A_1 \vec{I}\cdot\vec{S} + A_2 \vec{I}\cdot\vec{S},$$

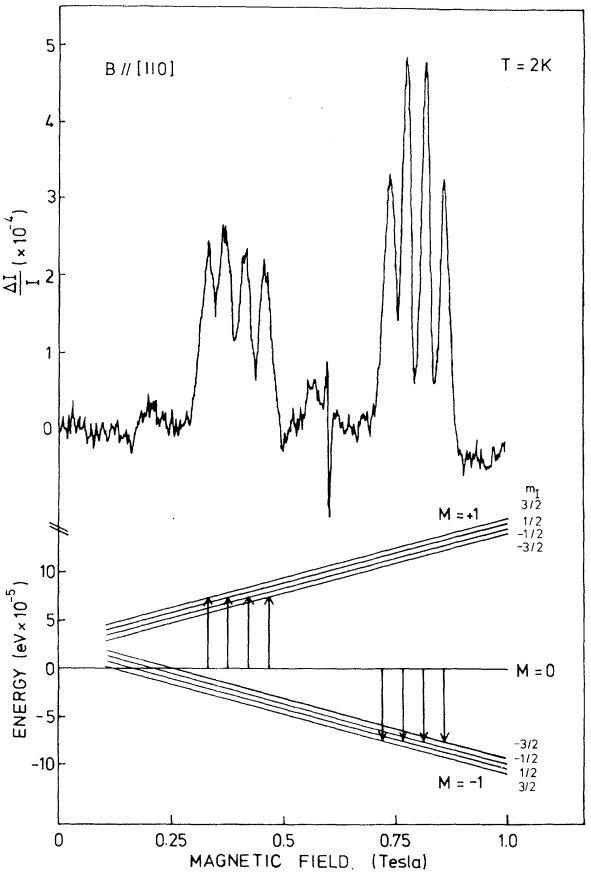

FIG. 2. Top: optically detected magnetic resonance of the O^- band at 16.5 GHz. Bottom: energy level scheme for a triplet in an axial field showing hyperfine interaction with one Ga nucleus. For the sake of simplicity an average hyperfine constant is illustrated instead of one for each Ga isotope.

where $S=1$ and D is the zero-field splitting constant. The hyperfine constants A_1 and A_2 describe the interactions between the electron spin and the ^{69}Ga and ^{71}Ga nuclei, each with $I=\frac{3}{2}$. Using the known isotopic abundancies, we used a line-fitting procedure of an expanded recording of the resonance to obtain the resonance parameters which, for the magnetic field in the [110] direction, are the following: $g_{\parallel}=2.011\pm0.005$, $D=+(2.32\pm0.01)\times10^{-5}$ eV. $A_1=(4.40\pm0.02)\times10^{-6}$ eV, and $A_2=(5.88\pm0.02)\times10^{-6}$ eV. The resonances are observed as increases in the total emission intensity which corresponds to the case for a triplet system where the spin relaxation time is longer than the radiative and nonradiative lifetimes and the population differences between Zeeman levels are determined by the different decay rates from these levels. In the present system the populations of the radiative $M=\pm1$ states drop below that of the $M=0$ state which has a long radiative lifetime because of the selection rules. Thus, at resonance the $|0\rangle\rightarrow|+1\rangle$ and the $|0\rangle\rightarrow|-1\rangle$ transitions will be observed.[12] The positive sign of D was determined from the polarization properties of the resonances; the high-field resonance was by a factor of 10 more intense for σ_- than σ_+ emission.

In order to determine the full symmetry of the O^- site, angular-dependence measurements have been carried out. The spectra are made more difficult to analyze, since in ODMR one has to take into account the effect of the magnetic-field orientation on the optical selection rules. If the magnetic field is applied at an angle to the crystalline axis, the states become mixed (by terms such as $g_{\perp}\mu_B\sin\theta S_x$) and the radiative transition from the $M=0$ state becomes allowed. Therefore, the population differences between the Zeeman levels depend on the angle between the crystalline axes and the magnetic field and thus not all expected resonance transitions are observed in the angular-dependence measurements. However, it is clear from our measurements that the principal distortion of the lattice is in the [110] direction but the precise determination of all the spin Hamiltonian parameters is very complicated and a full analysis of the magnetic resonance data will be published elsewhere.[13]

The optical detection of the level crossing between the $M=0$ and the $M=-1$ levels confirms the triplet nature of the energy level scheme. In the level-crossing experiment the magnetic field (being parallel to the [110] direction) is swept without the presence of the microwave field and an increase in the light intensity is observed at the crossing points of the $M=0$ and the $M=-1$ levels as can be seen in Fig. 3. This again is due to the mixing of the $M=0$ and the $M=-1$ states. The increase of the $|-1\rangle$ population at the level crossing increases the σ_- emission and also the σ_+ emission via the $(|+1\rangle)$-$(|-1\rangle)$ coupling.[14] The position of the level crossing is in good agreement with the energy diagram.

The observed interaction between the O^- state and a single Ga nucleus with $I=\frac{3}{2}$ can be explained if we suppose that when O^0 captures a second electron into the O^- excited state the lattice relaxes to a new equilibrium state which is characterized by an axial symmetry around the [110] direction and a strong interaction between the O^- atom and one of the Ga atoms. Such a spontaneous distortion of the local symmetry from tetrahedral to axial can be due to the Jahn-Teller effect, which lifts the orbital degeneracy of the triplet system. Another possibility could be a static deformation due to the presence of an interstitial impurity with $I=\frac{3}{2}$. This second hypothesis is, however, difficult to reconcile with the spectral dependence of the ODMR signals (see below).

We have studied the ODMR signals in different spectral regions by exciting luminescence with above-band-gap excitation. In those samples which showed the O^- band, the neutral O^0 to Zn, Cd, or C donor-acceptor emission bands showed similar resonances to the O^- band, but these res-

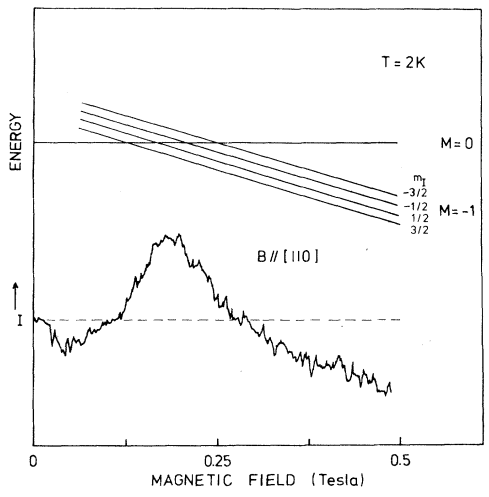

FIG. 3. Variation of the luminescence intensity of the O^- band as a function of magnetic field (level crossing). Also shown is the energy level scheme near the level crossing between the $M=-1$ and $M=0$ states.

onances were not observed in other samples. These results are consistent with our model. At resonance, the population of the triplet excited state decreases and that of the singlet ground state increases. The singlet state is expected to contain one electron in a localized state and one in an extended state.[7] This loosely bound electron can be annihilated by a nearby hole, leading to an increase in the neutral-O–donor population. Thus the same resonance is expected to be observed on the neutral-O^0–related emission bands. Since the O^0 state is known from several independent experiments to be a substitutional impurity, we exclude the possibility that the [110] distortion is due to the presence of an interstitial, as discussed above. This mechanism is further substantiated by the fact that we observed the same resonance on the emission of an exciton bound to a neutral Zn acceptor, but of opposite sign! This means that the number of neutral acceptors decreases following the resonance of the O^- state, which directly follows from the previous argument.

The above interpretation of the O^- band provides a simple explanation for the quenching of this band with increasing acceptor concentration[2] as well as for the absence of saturation of the O^- band under strong excitation.[2] (For a discussion, see Morgan, Ref. 7.) In addition, the absence of the zero-phonon transition in the absorption spectra[2] strongly suggests that it is a (spin-) forbidden transition, supporting the proposed model.

The sharp electron resonance at $g = 1.993$ ($B = 0.5916$ T) is observed as a decrease on all emissions but the linewidth and line shape depend on the excitation wavelength and so there are several contributions to this resonance. One likely possibility is that it is due to the spin-dependent capture of the second electron by the neutral oxygen center to become an O^- center.[15] Another possibility is that this resonance is related to a nonradiative center with spin-dependent electron capture.

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