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ESR of the doubly ionized Cr acceptor and infrared luminescence of Cr in GaP:Cr

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After optical excitation a broad isotropic electron-spin-resonance (ESR) signal with $g = 1.999$ has been observed in chromium-doped GaP. It is attributed to an isolated Cr^+ ($3d^5$) center, presumably on a Ga site, which may be viewed as the doubly ionized Cr acceptor. The low-energy threshold for optical Cr^+ generation is found to be at 1.15 eV. The Cr^+ generation is interpreted as electron excitation from the valence band into the singly ionized Cr acceptor, Cr^{2+} ($3d^4$). Photoluminescence (PL) measurements on GaP:Cr revealed an emission band with a sharp zero-phonon line at 1.03 eV followed by several phonon replicas. This PL is ascribed to the radiative capture of free (or loosely bound) carriers at one of the deep Cr centers. The similarity of the ESR and PL data for GaP:Cr and GaAs:Cr is demonstrated.

I. INTRODUCTION

Chromium doping of III-V semiconductors such as GaAs, InP, and GaP is known to produce semi-insulating material by compensation of residual shallow donors, e.g., Si and S. Despite the great technological importance of Cr-doped III-V compounds as substrates for device fabrication[1-3] the physical nature of the Cr center(s) controlling the electrical properties of the material has only recently become the subject of spectroscopic studies. Considerable progress in characterizing the Cr and other deep levels in GaAs was achieved by electrical, especially capacitance techniques.[4-7] However, most of these inherently macroscopic methods are incapable of unravelling the microscopic structure (charge state, lattice site, association effects) of the deep trap in question. Therefore a proper understanding requires the electrical data to be supplemented with microscopic information about the defect center involved. In this respect electron-spin-resonance (ESR) and luminescence measurements appear to be the most promising tools.

ESR studies of GaAs:Cr,[8-11] and of GaP:Fe,[12] have shown that Cr and Fe in III-V compounds may be present in multiple charge states rather than forming simple deep acceptors. The present ESR study of GaP:Cr has revealed a photosensitive ESR signal which is attributed to the doubly ionized Cr acceptor, Cr^+ ($3d^5$). Its generation and quenching with below-band-gap light suggests interconversion between Cr^{2+} and Cr^+, similar to the situation for GaAs:Cr.[8,9] The Cr^+ ion occupies an undistorted cubic site. This indicates that, at the doping levels studied (~1 at. ppm), complexing with other defects is of minor importance.

Recent work[13-16] on the 0.8-eV photoluminescence (PL) in GaAs:Cr has led to some controversy about the origin of this luminescence band. We believe that our observation of an analogous PL at 1.0 eV in GaP:Cr favors an interpretation in terms of radiative recombination of free carriers with one of the deep Cr centers. This is in contrast to the luminescence behavior of the deep iron centers in GaP and InP.[17,18] The PL bands observed in these cases undoubtedly arise from an internal *d-d* transition within the $3d^6$ configuration of Fe^{2+}.

II. EXPERIMENTAL

The crystals used in this study were grown by the liquid-encapsulation Czochralski (LEC) technique with 0.1-wt% Cr added to the melt. They were semi-insulating with dark resistivities in the range 10^4–10^{10} Ω cm at 300 K. The ESR measurements were performed with a Varian 35-GHz spectrometer using 100-kHz field modulation. *In situ* illumination of the samples was achieved through a quartz light pipe. PL spectra were measured with a Spex 0.75-m grating monochromator and a cooled PbS detector. The blue-green, yellow, and red lines of a krypton ion laser were used for excitation. The maximum power of the laser excitation was 500 mW.

III. RESULTS AND DISCUSSION

A. ESR

At 20 and 80 K, Cr-doped GaP exhibits an ESR spectrum very similar to that observed in GaAs:Cr.[8,9] The most prominent line in Fig. 1 appears only after excitation of the sample with light of energies greater

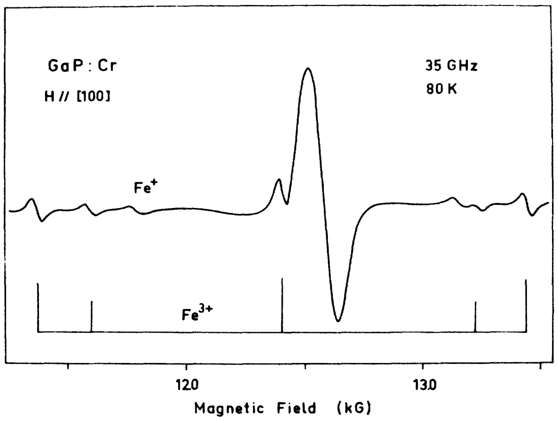

FIG. 1. ESR spectrum of Cr-doped semi-insulating GaP after illumination with near band-gap light. The intense, photoinduced central line is attributed to Cr^+ ($3d^5$).

than 1.15 eV. It is isotropic with $g=1.999$ and has a peak to peak width of about 130 G. We assign this signal to isolated Cr^+, presumably on a Ga site. The spectrum of Cr^{2+} recently identified in[19] GaAs and[20] InP was not detectable in our GaP:Cr samples at 20 K. This is not surprising since observation of this charge state usually requires temperatures below 20 K.[19,21]

Figure 2 shows the photo excitation band of the Cr^+ ESR signal. Its low-energy onset lies at 1.15 ± 0.07 eV. A steep rise in signal intensity occurs near 2.05 eV. The decrease in ESR intensity above $E_g=2.3$ eV is due to the fact that the excitation light penetrates only a small surface layer of the entire sample. After switching off the light the Cr^+ intensity decays to about half its light-on value within a few minutes at 80 K.

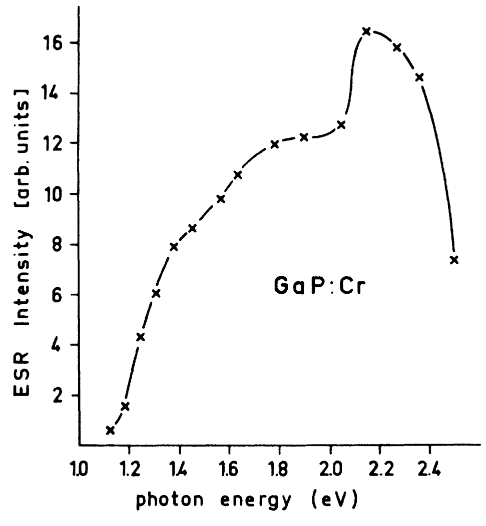

FIG. 2. Spectral dependence of the photoexcited steady-state Cr^+ ESR intensity. Measurements were performed with suitable interference filters under a constant photon flux. Before taking a new data point the sample was irradiated with 1.5-μm light in order to quench the Cr^+ intensity to its dark value (~0.5 on the ordinate scale).

If the sample is excited with the 633-nm He-Ne laser line in order to establish an equilibrium concentration of Cr^+ and simultaneously illuminated with a second light beam of longer wavelength, a substantial quenching of the Cr^+ ESR signal is observed. The quenching band extends down to about 0.5 eV. An almost 100% optical quenching is possible if the exciting light is switched off.

In addition to the Cr^+ signal, Fig. 1 also displays the well-known cubic Fe^{3+} ESR spectrum[22] as well as the signal of the double electron trap Fe^+.[12] Before illumination we also observed a weak spectrum due to cubic Mn^{2+}[23] For the data in Fig. 1, this spectrum is masked by the strong Cr^+ signal.

When the sample is cooled to 20 K in the dark none of the above mentioned spectra are observed. Instead there appears a weak complicated spectrum with orthorhombic symmetry which can be partially quenched by below band-gap light. For an arbitrary orientation of the magnetic field in a {110} plane up to 20 lines can be distinguished between 3 and 16 kG. One of these lines is the weak signal near 13.1 kG in Fig. 1. Our present data are insufficient to establish the origin of this spectrum, but it seems to be related to the Cr dopant.

The intense photoinduced signal in Fig. 1 was never observed in several non-chromium-doped GaP crystals but appeared in all of our Cr-doped samples. This strongly suggests that it arises from the Cr dopant. If one considers Cr^{3+}, Cr^{2+}, and Cr^+ as the possible charge states of Cr on a Ga site, then Cr^+, having a $3d^5$ configuration with ground state spin $S=\frac{5}{2}$, is the only charge state which can give rise to an ESR spectrum consisting of a single isotropic line with a very small negative g shift. This assignment is also supported by previous ESR data[24] on Cr^+ in $CdSiP_2$ where the impurity is coordinated by an almost regular P tetrahedron. Within the error limits the g factor of $CdSiP_2:Cr^+$ is identical to that observed here for $GaP:Cr^+$. The identification of the strong signal in Fig. 1 with Cr^+ implies that the typical five-line fine-structure pattern of such a $S=\frac{5}{2}$ center collapses into a single line due to the smallness of the fourth-order spin-Hamiltonian parameter a. In II-VI compounds the parameter a for Cr^+ is in the range 3–6 G.[25,26] For Cr^+ in $CdSiP_2$ it has a value of 6 G.[24] We therefore believe that the a parameter of Cr^+ in GaP is of the same order of magnitude. This readily explains the masking of any fine structure splitting by the large width of the individual lines.

In the following the mechanism responsible for the photoexcitation and quenching of the Cr^+ ESR spectra is discussed. The optical generation of Cr^+ can occur either via direct electron excitation from the valence band into Cr^{2+} or via an indirect process where some deep donor becomes ionized with subsequent trapping of the donor electron at Cr^{2+}. For two reasons the latter mechanism is considered less probable although we cannot rule out that it plays some minor role: (i) The most likely candidate for the deep donor in question is oxygen. The thresholds for ionization of the first and second donor electron from oxygen are near 0.85 and 1.6 eV,[27] respectively, at 167 K. These thresholds are distinctly different from the low-energy onset of the Cr^+ excitation in Fig. 2. (ii) The Coulomb repulsion between Cr^{2+} and a free electron does not favor electron capture at Cr^{2+}. If the direct ionization of Cr^{2+} is accepted to be the principal source for the Cr^+ generation it follows that the minimum energy required for exciting a valence electron into the Cr^{2+} center is 1.15 ± 0.07 eV. As in the case of GaAs:Cr this is very close to midgap.

The quenching of the Cr^+ ESR with additional ir light results from the conversion $Cr^+ \rightarrow Cr^{2+}$. In the case of GaAs:Cr it has been suggested[8] that the low-energy onset of this conversion is connected with the direct photoionization of an electron from Cr^+ to the conduction band. This interpretation is inadequate for GaP:Cr and also needs revision for GaAs:Cr. If the low-energy thresholds for Cr^+ excitation and Cr^+ quenching were both due to direct ionization processes, these thresholds should add to the band gap E_g. However, this sum is about 1.2 and 1.6 eV for GaAs and GaP, respectively, i.e., considerably less than the respective band gaps. This indicates that the low-energy onset of the Cr^+ quenching is connected with an indirect process: The holes released during Cr^+ excitation ($Cr^{2+} \rightarrow Cr^+ + \text{hole}$) are trapped by some unknown hole trap(s) deeper than 0.45 eV. These holes are freed by the quenching light and partly become retrapped by Cr^+. Indeed, the Coulomb attraction between a twofold negatively charged Cr^+ and a positive hole strongly favors hole trapping at Cr^+. It is also possible that the direct ionization of Cr^+ contributes to the quenching action of light with energies above 1.1 eV.

B. Infrared photoluminescence

At 6 K the PL spectrum of GaP:Cr exhibits a sharp zero-phonon line (ZPL) at 8303 cm^{-1} (1.03 eV) followed by a broad phonon sideband towards lower energies, see Fig. 3. This luminescence can be effectively excited with wavelengths (~650 nm) well below the band gap (~530 nm) of GaP. For comparison, Fig. 3 also shows the 0.8-eV PL band of GaAs:Cr (Refs. 13 and 14) which displays a ZPL at 6750 cm^{-1}. The details of phonon coupling in the GaAs spectrum have been discussed earlier.[13] The dominant sidebands arise from the $TA(X,L)$ and from the $LO(\Gamma)$ phonons. Essentially the same phonon side bands[28] appear in the GaP spectrum. Note that the total extent of both PL bands in Fig. 3 is roughly $3LO(\Gamma)$ and that the overall shape of the bands is very similar.

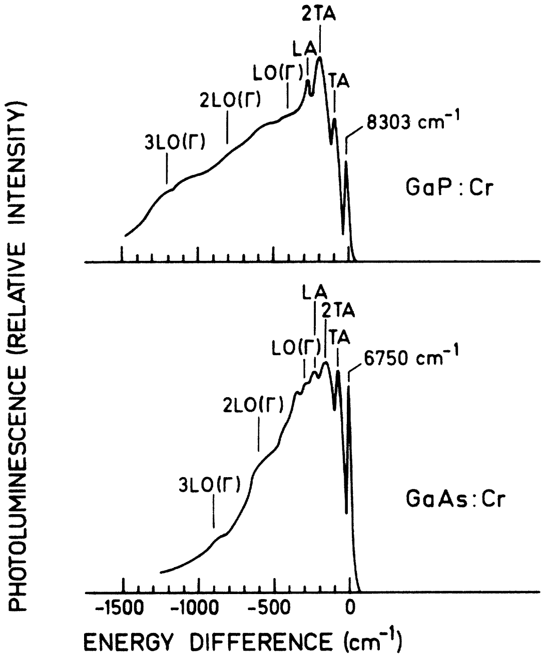

FIG. 3. Photoluminescence spectra of Cr-doped semi-insulating GaP and GaAs; $T \approx 6$ K.

Non-chromium-doped, LEC-grown GaP was investigated for comparison. In these samples the 1.0-eV luminescence could not be detected. This provides strong evidence that the luminescence is associated with the Cr dopant. The 1.0-eV spectrum in GaP has been observed previously by Dean,[29] but was not attributed to a specific defect or impurity. It was speculated that this luminescence might be connected with some stoicheometric defect or with some neutral exciton binding center. The first of these suggestions appears unlikely since the luminescence is associated with Cr doping. The second is ruled out by the observation that the luminescence can be effectively excited with light well below the band edge. The obvious similarity of the two bands in Fig. 3 suggests that the luminescence process responsible for the emission is the same in GaP:Cr and GaAs:Cr. The arguments given below are based on this assumption and on the experimental fact that the appearance of the bands involves the presence of Cr impurities.

Several explanations have been proposed for the 0.8-eV luminescence of GaAs:Cr but none of these has been firmly established: a conduction-band → neutral-acceptor and/or donor → acceptor transitions,[14,30] a hole → ionized-acceptor transition,[31] and a $^5E \rightarrow {}^5T_2$ crystal-field transition of Cr^{2+}.[13] In principle one also has to consider the possibility of a crystal-field transition between the first excited state $^4T_2$ and the ground state $^4T_1$ of Cr^{3+}. However, this alternative is considered unlikely because of the large energy difference between the band centers in GaAs and GaP, see Fig. 3. The same difficulties are encountered if the bands in Fig. 3 are attributed to the $^5E \rightarrow {}^5T_2$ crystal-field transition of Cr^{2+}. We therefore favor an assignment in terms of free (or loosely bound) carrier recombination with one of the deep Cr centers. The considerably larger ZPL energy in GaP is then a simple consequence of the larger depth of the luminescent Cr center in GaP as compared to GaAs.

The present PL data do not allow the identification of the charge states of the Cr center involved in the recombination process. It is also not clear whether electrons or holes are recombining with the deep Cr center in question.

Further studies of high-resolution spectra of GaP:Cr and GaAs:Cr at 2 K are in progress. Preliminary results indicate that the ZPL in GaP:Cr and GaAs:Cr (Fig 3) in fact consist of three and six lines, respectively. It is hoped that the analysis of this zero-phonon structure will help to clarify the above-mentioned questions.

IV. CONCLUSION

A combined ESR and luminescence study of chromium-doped GaP has revealed two deep levels associated with Cr. The first level at 1.15 eV corresponds to electron excitation from the valence band into the Cr^{2+} center. The doubly ionized Cr acceptor, thus created, is found to have cubic symmetry. The second 1.03-eV deep level (from either the conduction or the valence band) is associated with the capture of either electrons or holes at one of the deep Cr centers. Both the ESR and the optical results reported here on GaP:Cr are very similar to those obtained on GaAs:Cr.

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