New EPR data and photoinduced changes in GaAs:Cr. Reinterpretation of the "second-acceptor" state as Cr^{4+}

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Several samples with Fermi levels ranging from the valence to the conduction band show that the resonance previously attributed to Cr^{1+} is due to Cr^{4+}, and no additional signal is observed under conditions where Cr^{1+} would be expected to exist. The double-acceptor property postulated for Cr in GaAs is thus questionable. Depending on the Fermi-level location, two different spectra of light-induced changes in the Cr charge states are observed.

The existence of Cr in three different charge states in GaAs is now well recognized. It is important to the understanding of the action of Cr in compensating other impurities that these charge states be correctly identified. The states designated as $Cr^{3+} 3d^3$ and $Cr^{2+} 3d^4$ are unambiguously characterized by their EPR behavior.[1,2] The third state has always been less definitely established.[3,4] It is represented merely by a single featureless isotropic resonance line with g near 2 which indicates only that the ground state of the center is an orbital singlet in the tetrahedral symmetry of the Cr sites. There are two plausible charge states which satisfy this requirement, $Cr^{1+} 3d^5$ and $Cr^{4+} 3d^2$ which have $^6A_1$ and $^3A_2$ ground states, respectively. In GaP both of these states are thought to have been observed.[5] In this note we report new EPR results which indicate that the third charge state in GaAs previously designated Cr^{1+} should properly be identified as Cr^{4+}.[6] We also report a new variety of photoinduced changes in the charge states of Cr in GaAs.

The new data stem from examining bulk GaAs single crystals grown by the LEC (liquid-encapsulated Czochralski) method and codoped with Cr and either the shallow acceptor Zn or the shallow donor Sn. The nominal dopant concentrations are shown in Table I. Also shown are the Cr^{2+} and Cr^{3+} concentrations determined by EPR-optical methods.[7] At x band and 4.5 K sample 1, which is strongly p-type with a Zn concentration [Zn] $\gg$ [Cr], shows a very strong single isotropic EPR line in the dark with $g = 1.993 \pm 0.002$ and peak-to-peak derivative width $\Delta H = 123 \pm 2$ G; most importantly, it shows *no* Cr^{2+} or Cr^{3+} signals. The nature of the doping and the existence of high conductivity at 4.5 K indicate that the Fermi level is at or below the level of isolated Zn acceptors. Hence Cr^{1+} cannot be the source of this signal and we identify it as Cr^{4+}. Furthermore, based on a Cr^{4+} $S = 1$ assignment, we determine [4+] $= 7.9 \times 10^{16}$ cm^{-3} in this sample, which equals the total nominal Cr concentration. It is not possible to alter the Cr^{4+} signal in this sample with light.

Sample 2 is also p-type but with [Zn] < [Cr]. Portions 2A and 2B were taken from opposite ends of the boule. Since the state Cr^{4+} can exist, in such a sample we would expect [4+] = [Zn] − [D], [3+] = [Cr] − [4+], and no [2+] or [1+] in the dark. Here [D] is the concentration of any accidentally incorporated donors. The more conducting portion 2A shows this type of behavior (Table I), while 2B

TABLE I. GaAs samples. Concentrations in units of 10^{16} cm^{-3}.

Sample	Nominal doping			EPR calibration 4.5 K, dark			ρ at 295 K (Ω cm)
	[Cr]	[Zn]	[Sn]	[2+]	[3+]	[4+]	
1	8	44	· · ·	0	0	7.9	0.074−p
2A	> 8	> 5	· · ·	~0	16.7	4.3	224−p
2B	8	5	· · ·	~0.1	7.2	≤ 0.3	1950−p
3	10	· · ·	7	7.8	5 ± 3	0	5 × 10^8 − SI
4	6	· · ·	11	obs.	~0	~0	0.090−n

shows essentially all Cr in the 3+ state in the dark. Illumination with light at 0.9 μm induces [4+] $\cong 2.2 \times 10^{16}$ cm^{-3} in sample 2B and this state remains stable at 4.5 K after the light is removed. A measurement made on sample 2A at 24 GHz and 4.2 K gives $g = 1.994 \pm 0.001$ and $\Delta H = 112 \pm 2$ G for the isotropic line. This measurement verifies the stability of that signal in the dark, since the cavity was closed and immersed in liquid helium, thus eliminating the effects of room-temperature ir radiation which might occur with our x-band gas-flow cooler.[1] X-band data for sample 2B give the same g and ΔH values. We note that these values and the g of sample 1 are identical within experimental error to those assigned in the past to Cr^{1+}.[3,4] In samples 2A and 2B 0.9-μm light induces weak Cr^{2+} signals which can almost be eliminated by subsequent 1.6-μm illumination (cf. Fig. 1).

Sample 3 has [Sn] somewhat less than [Cr] and is semi-insulating (SI). Here we would expect [2+] = [Sn] + [D], [3+] = [Cr] − [2+], and no [4+] or [1+]. This is again in good agreement with the data (Table I). In this sample 0.9-μm light yields a very weak isotropic signal, consistent with the above parameters. Contrary to the cases of samples 2A and 2B, here it is the isotropic signal which can be quenched by 1.6-μm light. The corresponding light-on concentrations would be [4+] = 2×10^{14} or
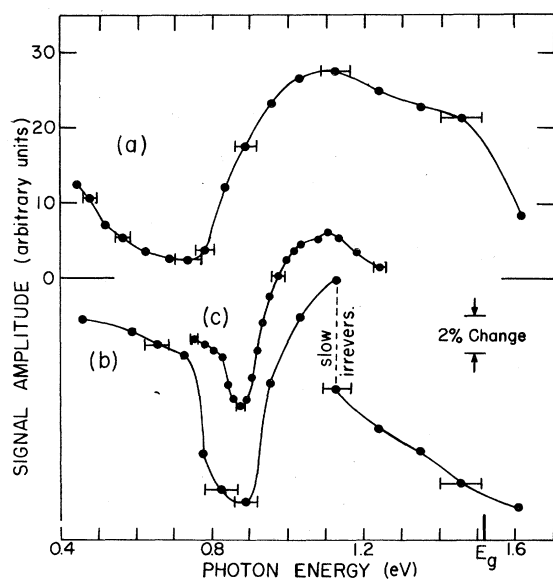

FIG. 1. Response of Cr^{2+} signal amplitude to ir illumination. (a) Sample 2B after initial illumination creating Cr^{2+}. (b) Initial low-to-high energy scan with a sample responding like sample 3. (c) Subsequent scan with same sample as (b) but at higher resolution. Note suppressed zero in (b) and (c). Illumination bandwidths shown are between zero intensity extremes.

[1+] = 5×10^{13} cm^{-3}. We emphasize that one must correct, as we have done, for possible microwave saturation in evaluating [4+] or [1+].

Finally, the fourth sample, with [Cr] = 6×10^{16} cm^{-3} and [Sn] = 1.1×10^{17} cm^{-3}, is n-type and too lossy for good EPR measurements. It is possible to observe a signal due to Cr^{2+} on a sloping background caused by magnetoresistive effects, but no trace of the isotropic line is found regardless of illumination. On this basis we can set an upper limit [1+] < [2+]/10. We note that a double-acceptor model allowing for the formation of Cr^{1+} predicts that this sample would show a strong Cr^{1+} signal and [1+] > [2+].

In the past we have observed the isotropic signal previously attributed to Cr^{1+} in many semi-insulating Cr-doped GaAs samples, but only during or shortly after excitation with light having $h\nu > 0.75$ eV. Our measurements show that the g parameter, linewidth, and even the microwave saturation behavior found for that signal are identical with the values found for Cr^{4+} in our new data. (In sample 1 the linewidth is slightly larger and saturation is significantly less; we credit this to the high conductivity of this sample.) We are thus led to conclude that, despite our previous support for the existence of Cr^{1+}, the proper identity of all the observed isotropic lines is a Cr^{4+} resonance and we have no EPR evidence for the occurrence of Cr^{1+} in GaAs.

The work of Brozel et al.[8] offered support for Cr^{1+}. This study used local-mode infrared absorption to calibrate the net concentration of Si donors and mass spectrometry to calibrate [Cr] for comparison with the concentration of free carriers. However, the recent local-mode work of Chen et al.[9] appears to undermine the basis of the Si calibration. On the other hand, the work of Ippolitova et al.,[10] which used straightforward radioactive tracer calibration methods, found a very sharp break from semi-insulating to conducting behavior just at the point where the number of added shallow donors (Sn) equaled the concentration of Cr. Hence the existence of a second deep acceptor state of Cr in GaAs seems doubtful. Photocapacitance studies by Szawalska and Allen[11] on Cr-doped GaAs have located a level closer to the conduction band than that of Cr^{2+}. We must consider its identity uncertain.

Identification of the isotropic EPR line with Cr^{4+} provides an immediate explanation for the results of Frick and Siebert.[12] These authors found that a heat treatment of GaAs:Cr which caused the isotropic EPR signal to become stable in the dark also enhanced the concentration of accidental Fe^{3+}. This can be interpreted simply as the result of lowering the Fermi level.

In the course of this work we have found that Cr-doped GaAs samples with [2+] > [3+] show a response to light related to that reported in photoconductivity,[13] i.e., a resonancelike dip in [2+] at 0.87

eV, a broad maximum at about 1.1 eV (where first-time irreversibilities are pronounced), and a subsequent decrease to the band edge. This spectral dependence is quite different from that described earlier,[1,2,4] in which a strong midgap transition is the dominant feature and $[3+] > [2+]$. These two types of Cr^{2+} response are shown in Fig. 1. The new type of photoresponse is weak enough that it can be masked when the midgap transition is strong. The variation in the relative strengths of the two light-induced processes with the charge state of Cr is similar to that observed in optical absorption.[10] In the context of the $4+-3+-2+$ system, we interpret the low-energy (0.45–0.7 eV) decrease in $[2+]$ as resulting from the process $Cr^{4+} + Cr^{2+} \xrightarrow{h\nu} Cr^{3+} + h$ $+ Cr^{2+} \rightarrow 2Cr^{3+}$. The decrease in Cr^{4+} and increase in Cr^{3+} in this model are in fact observed. The midgap transition represents most likely the process $Cr^{3+} \xrightarrow{h\nu} Cr^{2+} + h$ where the hole generated is free to create the observed additional Cr^{4+}. At 0.87 eV the competing resonant effect reflects $Cr^{2+} \xrightarrow{h\nu} Cr^{3+} + e$; when strong enough, this causes an increase in Cr^{3+} which is seen, as well as a significant increase in conductivity.[14]

There are three main consequences of the above discussion for the work which we have reported previously on Cr in GaAs:

(1) The state identified in the past as Cr^{1+} is most probably Cr^{4+} and we have no compelling evidence for the existence of a Cr^{1+} state. Hence, the postulated double-acceptor property of Cr must be questioned.

(2) Our method[7] for the EPR determination of Cr charge state concentrations remains valid. In semi-insulating samples Cr^{4+} is not a stable state. However, the Cr^{4+} produced by illumination must be accounted for in the calibration. Because the EPR sensitivity is less for Cr^{4+} than for Cr^{1+}, any light-induced signal observed is correspondingly more significant (in the ratio $\frac{35}{8}$). The calibration method depends on the production of significant population changes through illumination. For samples with a strong midgap response 1.6- and 0.9-μm irradiations are appropriate.[7] However, in samples without much midgap response a more effective pair is 1.4 and 1.1 μm.

(3) The light-induced effects used previously[4] to support the identification of Cr^{1+} are equally compatible with Cr^{4+}. However, the model system suggested[15] to account for the recovery of signals following photoexcitation must be changed. Similar nonlinear rate equations can be constructed for the Cr^{4+}-Cr^{3+}-Cr^{2+} system, but the necessity for an additional center 0.45 eV above the valence band now seems weaker. The 0.45-eV transition may be due to the conversion of Cr^{4+} to Cr^{3+} via excitation of a valence-band electron. The random variation in Cr-Cr spacing and tunneling between Cr centers may be sufficient to account for the behavior observed.[14]

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