Properties of Cr deep levels in Al$_x$Ga$_{1-x}$As:Cr

K. Kocot,* R. A. Rao,† and G. L. Pearson

Stanford Electronics Laboratories, Stanford University, Stanford, California 94305

Studies have been conducted which clarify the mechanism producing the 0.8-eV photoluminescent band in Al$_x$Ga$_{1-x}$As:Cr. Photocapacitance was employed to measure the optical ionization energies of Cr^{2+} with respect to the conduction and valence bands as a function of composition x. It was shown that the sum of the optical ionization energies of Cr^{2+} exceeds the direct energy gap by an amount ΔE, the magnitude of which decreases with increase in x. An explanation of this result is given in terms of the conduction-band structure and Stokes' shift. Photoconductivity measurements were carried out which establish the degeneracy range of the Cr^{2+}(^5E) excited level with respect to the conduction band as x is varied from 0 to 0.6. Alternate models of photoluminescent intraimpurity transitions from Cr levels in n- and p-type crystals are analyzed.

I. INTRODUCTION

Gallium arsenide doped with Cr has been the subject of numerous investigations[1-5] because of its great technological importance. However, the physical nature of the Cr centers has not been firmly established. The AlGaAs:Cr system may have even greater technical importance [e.g., as the semi-insulating material in metal insulator semiconductor (MIS) field-effect transistor devices].

Photoluminescent studies on Al$_x$Ga$_{1-x}$As:Cr single crystals at 77 K have shown[6,7] that the Cr^{2+} band located at 0.8 eV is independent of Al composition x. This result led us to conclude that this band arises from internal transitions between the ^5E excited state and the $^5T_2$(Cr^{2+}) ground level. The present study was undertaken in order to determine the energy level diagram of the Al$_x$Ga$_{1-x}$As:Cr system and to obtain further experimental evidence concerning the nature of the photoluminescent transitions which produce the 0.8-eV band.

II. CRYSTAL GROWTH

The Al$_x$Ga$_{1-x}$As:Cr single crystal layers were grown on (100) GaAs substrates using liquid-phase epitaxial (LPE) techniques. High quality crystals of the desired composition ($0 < x < 0.6$) were prepared by adding the required amount of Al to As-saturated Ga melts as specified by the phase equilibria data of Panish and Ilegems.[8] Semi-insulating crystals were obtained by adding 0.5 mole% Cr to the melt and n- or p-type layers were grown by doping with Sn or Ge.

Prior to growth, the melts were baked out for 50 h at 800 °C in flowing H$_2$ to remove residual impurities. The melt was then placed on the substrate and an LPE layer, $\approx$5-μm thickness, was grown as the system cooled from 800 to 785 °C. Terminating the growth cycle at 798 °C, provided $\approx$0.5-μm layers. The semi-insulating layers had differential resistivities in the 10^{10} Ω cm range at 1 V, and the carrier concentration in the Sn or Ge doped layers was adjusted to $1-5 \times 10^{16}$ cm^{-3}.

III. PHOTOCAPACITANCE MEASUREMENTS

Electron-spin resonance studies[9-11] have shown that Cr can be present in three different charge states in GaAs. These include Cr^{3+}, Cr^{2+}, and Cr$^+$ ions which are in order (i) neutral, (ii) single negatively and (iii) double negatively charged with respect to the lattice.

Photocapacitance measurements were carried out in order to determine the location of the Cr^{2+} ground level within the energy gap of Al$_x$Ga$_{1-x}$As:Cr and its dependence on composition x. A double source photocapacitance technique, as described by White et al.,[12] was used for this purpose. Schottky barrier diodes were prepared by evaporating small Au dots on (n)Al$_x$Ga$_{1-x}$AS:Cr single-crystal layers and breaking down one of the dots to form an ohmic contact.

The sample was irradiated simultaneously with light at both the prime and probe energies. The prime energy was fixed slightly below the band gap while the probe energy was varied to excite the various levels under investigation (0.7 to 2.2 eV in our studies). The prime light creates a fixed population of holes on the Cr^{2+} levels which, in accordance with the transition probabilities and relevant rate equations, produces a steady state capacitance. This capacitance is altered as the second light source (probe radiation) is swept from low to high energies. Above the ionization energy of Cr^{2+} or Cr^{3+} the probe light upsets the steady state populations by transfer of carriers to the conduction or valence band, respectively. These carriers are swept away by the electric field at the depletion region, thus altering the space charge distribution so that the capacitance changes to a

new value, greater or smaller according to whether the transitions are to the conduction or valence band.

A typical photocapacitance spectrum of an n-type $Al_xGa_{1-x}As:Cr$ crystal is shown in Fig. 1 as measured at 85 K. Two thresholds are observed which we assign to Cr levels. This assignment is based on the fact that the thresholds appear only in Cr doped samples, and that they are located in the expected energy range. The negative change of capacitance corresponds to transition of holes from the Cr^{3+} level to the valence band, and its threshold gives the position of the Cr^{2+} level with respect to the top of the valence band. The positive change of capacitance corresponds to the transfer of electrons from the Cr^{2+} level to the conduction band and its threshold gives the location of the Cr^{2+} level with respect to the conduction band. The measured value is dependent on the relative positions of the Γ and L minima as will be discussed in Sec. V.

The thresholds of electronic transitions from the Cr^{2+} ground level to the conduction band are shown in Fig. 2(a) for crystals having different values of x. It is seen that the optical ionization energies vary from 0.80 to 1.00 eV when x varies from 0 to 0.42. Figure 2(b) shows the thresholds of hole transitions from the Cr^{2+} ground level to the top of the valence band as obtained from the same set of crystals. In this case the optical ionization energies vary from 0.90 to 1.20 eV. A summary of the data together with the Γ and L band gap energies are given in Table I.

It is to be noted that the sum of the ionization energies at each value of x exceeds the direct bandgap E_g^Γ by an amount ΔE. This excess, as plotted versus crystal composition in Fig. 3, decreases with x but levels off around 0.3. This behavior will be discussed in Sec. V.
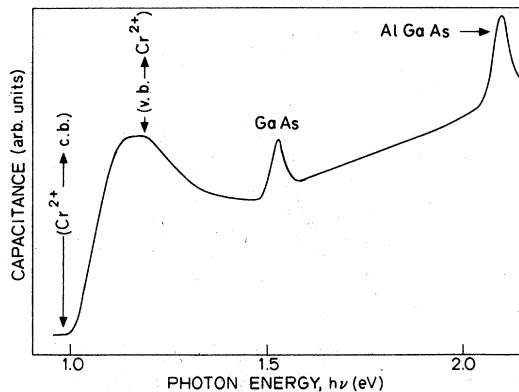
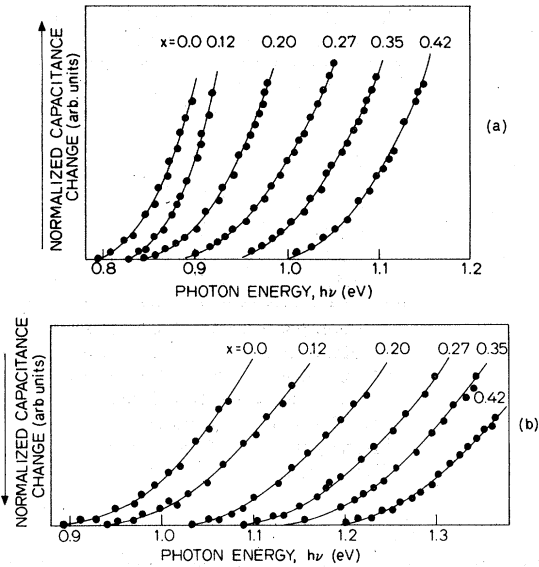FIG. 1. Photocapacitance spectrum of n-type $Al_{0.42}$ $Ga_{0.58}As:Cr$ at 85 K. The structure between 1.0 and 1.3 eV arises from the Cr^{2+} level.

FIG. 2. Photoionization thresholds of the Cr^{2+} level in (n) $Al_xGa_{1-x}As:Cr$. (a) Conduction band and (b) valence band. Note that the ordinate scale is reversed in (b).

Similar photocapacitance measurements were carried out on p-type crystals. Since it was impossible to make satisfactory Schottky barriers on this material, the measurements were made on grown $(p)Al_xGa_{1-x}As:Cr - (n^+)GaAs$ heterojunctions. Thresholds were observed at the same energies as
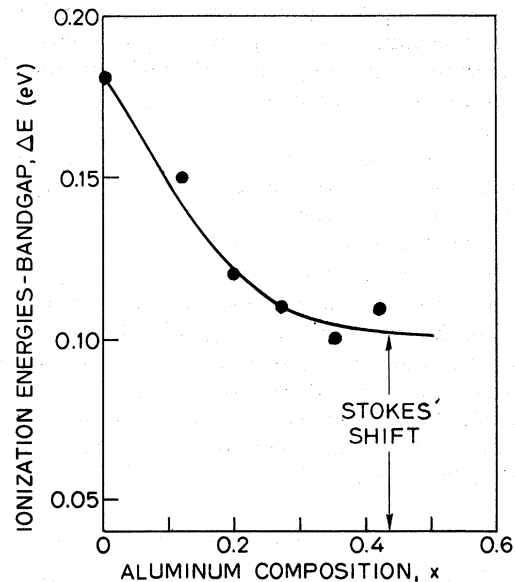
FIG. 3. Sum of the optical ionization energies of Cr^{2+} minus the band gap energy vs x.

TABLE I. Optical ionization energies of Cr with respect to the valence and conduction bands at 85 K. (All energies are given in electron volts.)

x [a]	Cr^{2+} − valence band [b]	conduction band − Cr^{2+} [c]	ΣE_I [d]	E_g^{Γ} [e]	E_g^{L} [f]	ΔE [g]
0	0.90	0.80	1.70	1.52	1.71	0.18
0.12	0.99	0.83	1.82	1.67	1.79	0.15
0.20	1.04	0.85	1.89	1.77	1.84	0.12
0.27	1.09	0.89	1.98	1.87	1.89	0.11
0.35	1.14	0.94	2.08	1.98	1.93	0.10
0.42	1.20	1.00	2.20	2.09	1.98	0.11

[a] Al composition of Al$_x$Ga$_{1-x}$As:Cr crystal.
[b] Ionization energy of Cr^{2+} with respect to the valence band.
[c] Ionization energy of Cr^{2+} with respect to the conduction band.
[d] Sum of the ionization energies.
[e] Band gap at the Γ point.
[f] Band gap at the L point (295 K).
[g] $\Sigma E_I - E_g^{\Gamma}$.

in n-type Al$_x$Ga$_{1-x}$As:Cr, but the direction of capacitance change was reversed. Increase of capacitance in p-type crystals is caused by hole emission from the Cr^{2+} center, while transitions from the Cr^{2+} level to the conduction band (electron emission) are observed as a decrease in capacitance.

IV. PHOTOCONDUCTIVITY MEASUREMENTS

Photoconductivity measurements were carried out in order to determine the composition range in which the Cr^{2+}(^5E) excited level is degenerate with the conduction band and also to verify the optical ionization energies obtained from our photocapacitance measurements.

N-type Al$_x$Ga$_{1-x}$As:Cr LPE layers with selected Al compositions were grown on high resistivity *undoped* GaAs substrates. Ohmic contacts were applied to the conduction layer by alloying In pellets.

The photoconductivity spectra shown in Fig. 4 were recorded from crystals having compositions $0.0 \leqslant x \leqslant 0.6$. The peaks centered around 0.95 eV are due to $^5T_2$(Cr^{2+}) → ^5E transitions; those at 1.5 eV are from band-to-band transitions in the GaAs substrate and those at higher energies from band-to-band transitions in the AlGaAs layer. Note that the Cr peaks are present in crystals with $x = 0$, 0.12, and 0.23 but are absent when $x = 0.38$ and 0.60. The ^5E excited level must therefore be within the conduction band when $x \leqslant 0.23$ and within the band gap when $x \geqslant 0.38$.

V. DISCUSSION

This section will discuss the dependence of the ionization energies of Cr^{2+} on Al composition, the degeneracy of the ^5E(Cr^{2+}) excited level, and alternate models for describing photoluminescent

intraimpurity transitions in AlGaAs:Cr.

It was mentioned in Sec. III that the sum of the optical ionization energies with respect to the valence and conduction bands exceeds the direct energy gap by an amount ΔE. The relationship be-
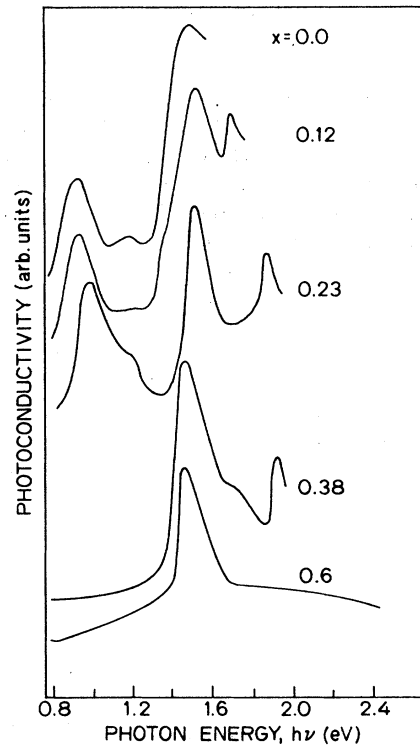

FIG. 4. Photoconductivity spectra of (n)Al$_x$Ga$_{1-x}$As:Cr at 85 K. The peaks located near 0.95 eV are due to Cr^{2+} internal transitions.

tween ΔE and Al compositions x, as shown in Fig. 3, can be explained by the conduction band structure of $Al_xGa_{1-x}As:Cr$ after taking the Stokes shift into account. The L minimum is 0.19 eV above the Γ minimum in GaAs. The Cr level is highly localized in real space and hence is delocalized (spread out) in k space so that optical transitions are possible to the L minimum. Since the density of states in the Γ minimum is much smaller than in the L minimum, only the higher-energy regions of the valley contribute to the photocapacitance change. Even at $x = 0$ the change of capacitance as a result of transitions to the L minimum is larger than that due to transitions to the Γ minimum. As x increases, the Γ minimum moves up in energy faster with respect to the valence band than the L minimum and both have approximately the same value at $x = 0.4$. Beyond this point $Al_xGa_{1-x}As:Cr$ becomes an indirect gap material. It thus follows that the energy involved in optical transitions from the Cr^{2+} ground level to the conduction band should increase rapidly at first as x increases from zero but approach a constant value as we approach and pass $x = 0.4$.

The DLTS measurements of Lang and Logan on GaAs:Cr[13] have shown that the *thermal* ionization energy of transitions from Cr^{2+} to the bottom of the conduction band is 0.61 eV. Hence, at $x = 0$, the energy involved in optical transitions into the conduction band should have an intermediate value between 0.61 eV (Γ valley) and 0.80 eV (L valley) which is consistent with the value of 0.80 eV ($\Delta E = 0.18$ eV) given in Table I. Based on these considerations, ΔE is expected to approach 0 as x approaches 0.4. However, a contribution from the Stokes shift causes ΔE to level off at 0.1 eV as indicated in Fig. 3. It should be noted that the thermal excitation energy of GaAs:Cr plus its optical ionization energy to the top of the valence band is equal, as expected, to the direct bandgap energy ($E_g^{\Gamma} = 1.52$ eV at 85 K).

From the above analysis and the experimental results presented in this paper, we have drawn the energy level diagram shown in Fig. 5. The solid data points give the position of the $^5T_2(Cr^{2+})$ ground level with respect to the conduction band as obtained from photocapacitance thresholds, and the open circles indicate the energy position of the ^5E excited level as obtained from photoconductivity peaks. The dashed portion of the curve has been extrapolated beyond the region where measurements were possible. It can be seen that the $Cr^{2+}(^5E)$ excited level is a resonant state (degenerate) in $Al_xGa_{1-x}As:Cr$ crystals when x is less than ≈ 0.35 but is a discrete state (a state lying within the band gap) when x is greater than this value.
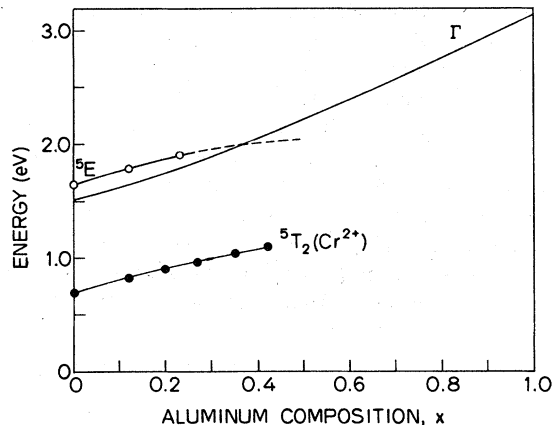

FIG. 5. Energy level diagram of $Al_xGa_{1-x}As:Cr$. ● from photocapacitance data, o from photoconductance data—extrapolation.

The results presented in Ref. 6 together with the photocapacitance and photoconductivity data given above prove that the 0.8-eV photoluminescent peak in $Al_xGa_{1-x}As:Cr$ is due to intraimpurity transitions.

The models shown in Fig. 6 are proposed to explain internal field transition in both n- and p-type AlGaAs:Cr crystals. The Cr atoms occupy Ga or Al sites and therefore appear in the 3+ charge state in high purity crystals. However, compensation exists in n-type material containing shallow donors which converts Cr to the 2+ charge state. Electrons are excited from the $Cr^{2+}(^5T_2)$ ground level to the conduction band by laser light to produce Cr in the 3+ charge state and an electron in the conduction band. The Cr^{3+} center then captures
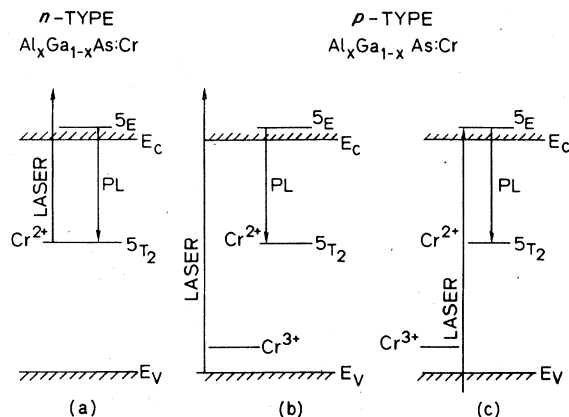

FIG. 6. Possible excitation mechanisms of photoluminescence in n- and p-type $Al_xGa_{1-x}As:Cr$ crystals based on crystal-field theory.

an electron to produce a Cr^{2+} center in the ^5E excited state which decays radiatively to emit the photoluminescent signal as shown in Fig. 6(a).

In p-type AlGaAs:Cr, electrons are excited from the valence to the conduction band and then captured by the Cr^{3+} centers to produce a Cr^{2+} center in the ^5E excited state which, as in n-type crystals, decays radiatively to give the 0.8-eV photoluminescent peak [Fig. 6(b)]. A second mechanism is also possible in p-type crystals. Electrons are excited by the laser light from within the valence band to the ^5E excited state of Cr^{2+} and then decay radiatively to the $^5T_2$ ground level to produce the photoluminescent peak as shown in Fig. 6(c). Probably each of the described mechanisms contributes to the 0.8-eV photoluminescent band in p-type AlGaAs:Cr.

ACKNOWLEDGMENT

*Present address: Institute of Experimental Physics, Warsaw Univ., Hoza 69, Warsaw, Poland.

†Present address: Dept. of Electrical Engineering, San Jose State Univ., San Jose, Calif. 95192.

[1] W. H. Koschel, S. G. Bishop, and B. D. McCombe, Solid State Commun. 19, 521 (1976).

[2] A. L. Lin and R. M. Bube, J. Appl. Phys. 47, 1959 (1976).

[3] H. J. Stocker and M. Schmidt, Proceedings of the Thirteenth International Conference on the Physics of Semiconductors (Tipografia Marves, Rome, 1976), p. 611.

[4] E. C. Lightowlers and C. M. Penchina, J. Phys. C 11, L405 (1978).

[5] L. Instone and L. Eaves, J. Phys. C 11, L771 (1978).

[6] K. Kocot and G. L. Pearson, Solid State Commun. 25, 113 (1978).

[7] V. F. Kovalenko, F. P. Kesamanly, J. E. Maronchuk, B. P. Masenko, G. P. Peka, and L. G. Shepel, Sov. Phys. Semicond. 11, 1303 (1977).

[8] M. B. Panish and M. Ilegems, in Progress in Solid-State Chemistry, edited by H. Reiss and J. O. McCladin (Pergamon, Oxford, England, 1972), p. 39.

[9] V. Kaufmann and J. Schneider, Solid State Commun. 20, 143 (1976).

[10] G. H. Strauss and J. J. Krebs, in Gallium Arsenide and Related Compounds (Edinburgh), 1976 (Institute of Physics Conference Series No. 33a, Bristol and London, 1977), p. 84.

[11] J. J. Krebs and G. H. Strauss, Phys. Rev. B 15, 17 (1977).

[12] A. M. White, P. J. Dean, and P. Porteous, J. Appl. Phys. 47, 3230 (1976).

[13] D. V. Lang and R. A. Logan, J. Electron. Mater. 4, 1053 (1975).