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Positive Identification of the $\text{Cr}^{4+} \rightarrow \text{Cr}^{3+}$ Thermal Transition in GaAs

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Temperature-dependent Hall-effect measurements on two Cr-doped GaAs samples show a dominant center at $E_1 = 0.324 - 1.4 \times 10^{-4}T$ eV, with respect to the valence-band edge. By comparison with secondary-ion mass spectroscopy measurements of the Cr concentration, and recent EPR measurements of the Cr^{2+} , Cr^{3+} , and Cr^{4+} concentration in several samples, it is shown unambiguously that this energy describes the $\text{Cr}^{4+} \rightarrow \text{Cr}^{3+}$ transition. This is the first conclusive evidence for a charge-state transition involving Cr^{4+} in GaAs.

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The discovery, in 1964, that Cr doping could make GaAs semi-insulating (SI)¹ has stimulated numerous investigations of this system. Evidence suggests that the Cr enters the lattice on a Ga site, using three of its outer-shell electrons for tetrahedral bonding. Thus, in the EPR notation, the neutral configuration is $\text{Cr}^{3+}(3d^3)$, but a donor state $\text{Cr}^{4+}(3d^2)$, and two acceptor states, $\text{Cr}^{2+}(d^4)$ and $\text{Cr}^{1+}(d^5)$, have also been observed.²⁻⁵ The transitions between these states are, naturally, of high importance, from both practical and academic points of view. Of the three possible transitions involving the addition of an electron from the valence band, only the $\text{Cr}^{3+} \rightarrow \text{Cr}^{2+}$ case has been extensively studied, by both electrical (thermal) and optical-absorption techniques. It is this transition, of course, that produces SI GaAs. Recent results give $E_2^{\text{therm}} = 0.838 - 2.6 \times 10^{-4}T$ eV,⁶ and $E_2^{\text{opt}} = 0.831 - 2.8 \times 10^{-4}T$ eV,⁷ where $E_2 \equiv E(\text{Cr}^{3+} \rightarrow \text{Cr}^{2+})$.

The other two transitions, $\text{Cr}^{4+} \rightarrow \text{Cr}^{3+}$ and $\text{Cr}^{2+} \rightarrow \text{Cr}^{1+}$, are much more difficult to observe. For the $\text{Cr}^{2+} \rightarrow \text{Cr}^{1+}$ case, it has recently been found⁴ that $E_3^{\text{therm}}(295 \text{ K}) = 1.54$ eV with a temperature coefficient, from 77 to 300 K, of about -8×10^{-5} eV/K. (Note that this level is in the conduction band.) For the $\text{Cr}^{4+} \rightarrow \text{Cr}^{3+}$ transition, no thermal measurements have been carried out, while recent photo-EPR^{2,3} and photoconductivity^{7,8} results suggest that $E_1^{\text{opt}} \approx 0.42 - 0.45$ eV from the valence-band edge. However, it should be pointed out that in these optical experiments there is no proof that Cr^{4+} is directly involved, although it is a reasonable assumption. In this paper, we give conclusive evidence for the involvement of Cr^{4+} in a transition, namely in the thermal tran-

sition, $\text{Cr}^{4+} \rightarrow \text{Cr}^{3+}$.

In Fig. 1 we present temperature-dependent Hall-effect measurements for a *p*-type GaAs:Cr, Zn sample, 781/9. This crystal and another, 781/5, were measured over the range 140–660 K. The hole concentrations were calculated from the relationship $p = (eR)^{-1}$, where R is the Hall coefficient and e , the electronic charge. The Hall scattering factor has been set equal to unity, since that is considered a reasonable estimate for all III-V compounds,⁹ and since, in any case, a complete calculation for GaAs, including all important scattering mechanisms, has not been carried out. The Hall-effect data were fitted by using a completely general charge-conservation equation, as given by Look.¹⁰ From Eq. (40) of

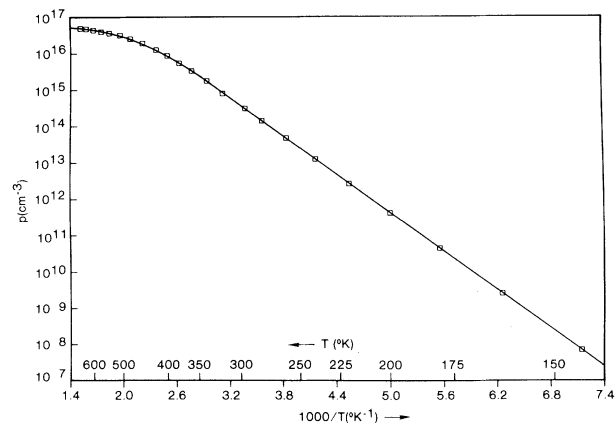


FIG. 1. Hole concentration vs inverse temperature for GaAs sample 781/9. Squares are experimental points. Solid line is theoretical fit with Eq. (5), text, with parameters as given in Table II.

Ref. 10 it can be shown that

$$n = p + \sum_{k,l,m} (l_k - l) n_{klm}, \quad (1)$$

where k includes all donors and acceptors in the system, l_k is the number of *donor* states of the k th defect or impurity, the index l runs from 0 to the *total* number of donor plus acceptor states of the k th center, the index m runs over all excited states, and

$$n_{klm} = N_k \left(1 + \sum_{l',m' \neq l,m} \frac{g_{kl'm'}}{g_{klm}} \exp \left[\frac{\epsilon_{klm} - \epsilon_{kl'm'} - (l-l')\epsilon_F}{kT} \right] \right)^{-1}. \quad (2)$$

Here g_{klm} is the degeneracy of the (klm) th state, ϵ_{klm} is its energy, and ϵ_F is the Fermi energy, with all energies measured with respect to the valence band. The summation restriction means that $l' \neq l$ and $m' \neq m$, *at the same time*. Note that ϵ_{klm} is the energy necessary to add l electrons, in the m th excited state, to a center of type k , which originally had $l=0$, i.e., $\epsilon_{k0} = 0$. We must distinguish this energy definition from that of the *ionization* energy, which is $E(l-l+1) \equiv \epsilon_{k(l+1)} - \epsilon_{kl}$, the experimentally measured quantity.

Now Cr in GaAs exhibits one donor state, Cr^{4+} , and two acceptor states, Cr^{2+} and Cr^{1+} . Thus, $l_k = 1$, and $l = 0, 1, 2, 3$. The ground-state terms are given in Refs. 2, 3, 11, and 12, and the degeneracies are immediately obvious from these terms: $g_0(4+) = 3$, $g_1(3+) = 4$, $g_2(2+) = 5$, and $g_3(1+) = 6$. Here we have disregarded spin-orbit splittings, which are much smaller than kT ,^{11,12} at least over the range of this experiment, $140 \leq T \leq 660$ K. Also, the higher term states are at energies much greater than kT , so that no summations over excited states (index m) need be carried out at all. Finally, we will not include the Cr^{1+} configuration ($l=3$) in our summation, since, at standard pressure, the ground state is evidently slightly above the conduction-band edge,⁴ thus making this configuration unstable (except, perhaps, for highly degenerate n -type samples). Equation (1) then becomes

$$\begin{aligned} n &= p + N_{DS} - N_{AS} + \frac{N_{\text{Cr}}}{1 + (g_1/g_0) \exp[-(\epsilon_1 + \epsilon_F)/kT] + (g_2/g_0) \exp[-(\epsilon_2 + 2\epsilon_F)/kT]} \\ &\quad - \frac{N_{\text{Cr}}}{1 + (g_0/g_2) \exp[(\epsilon_2 - 2\epsilon_F)/kT] + (g_1/g_2) \exp[(\epsilon_2 - \epsilon_1 - \epsilon_F)/kT]} \\ &= p + N_{DS} - N_{AS} + N_{\text{Cr}}^{4+} - N_{\text{Cr}}^{2+}. \end{aligned} \quad (3)$$

Here N_{DS} (N_{AS}) is the concentration of all donors (acceptors) more than a few kT above (below) the Fermi level. It is assumed that there are no *significant* concentrations of donors or acceptors (besides Cr, of course) within a few kT of the Fermi level. (If so, the data obviously will not be well fitted without the consideration of such centers.) For samples 781/5 and 781/9, several of the terms in Eq. (3) can be ignored. Then, by using the *ionization* energies, $E(4+ \rightarrow 3+) \equiv E_1 = \epsilon_1 - \epsilon_0 = \epsilon_1$, and $E(3+ \rightarrow 2+) \equiv E_2 = \epsilon_2 - \epsilon_1$, and also $p = N_v \exp(-\epsilon_F/kT)$, we get

$$0 = p + N_{DS} - N_{AS} + \frac{N_{\text{Cr}}}{1 + p^{-1}[(g_1/g_0)N_v \exp(-E_1/kT)]}, \quad (4)$$

where $N_v = 1.66 \times 10^{15} T^{3/2} \text{ cm}^{-3}$, the valence-band effective density of states.¹³ The terms involving E_2 are not important here, although they dominate, of course, for SI samples.

The best values for the four relevant parameters [N_{Cr} , $N_{DS} - N_{AS}$, E_{10} , and $(g_1/g_0) \exp(\alpha/k)$] were determined by a general, least-squares minimization technique, and are presented in Table I. Here, α is defined by $E_1 = E_{10} - \alpha T$. The value of α for each sample was determined by assuming $g_1/g_0 = \frac{4}{3}$, certainly a reasonable assumption over the temperature range of the experiment, as discussed earlier. Thus, the energy can be written as

$$E_1 \equiv E(4+ \rightarrow 3+) = [(0.324 \pm 0.002) - (1.4 \pm 0.3) \times 10^{-4} T] \text{ eV}, \quad 140-660 \text{ K}, \quad (5)$$

with respect to the valence-band edge. For sample 781/5, which was a small chip from near the wafer edge, the accuracy is poorer, because of more data scatter. However, the results are consistent, as seen in Table I. We may note that a significantly poorer fit was obtained for both samples by attempting to linearize the temperature variation of E_1 with respect to the *conduction*-band edge, rather

TABLE I. Curve-fitting parameters for temperature-dependent Hall-effect data. Also, SIMS results for N_{Cr} compared.

Sample	N_{Cr} (10^{16} cm^{-3})	(N_{Cr} : corr. SIMS) ^a	$N_{AS} - N_{DS}$ (10^{16} cm^{-3})	$E(4+ \rightarrow 3+)$, $T=0$ (eV)	(g_1/g_0) $\times \exp(\alpha/k)$	α (10^{-4} eV/K) ^b	$\chi_{\min}^{\text{best c}}$
781/5	7 ± 2	(6.8)	6 ± 3	0.332 ± 0.008	$3 \pm \frac{8}{2}$	1 ± 1	2×10^{-3}
781/9	8.5 ± 0.8	(8.5)	5.6 ± 0.5	0.324 ± 0.002	$6.4 \pm \frac{3.5}{1.9}$	1.4 ± 0.3	2×10^{-4}

^aCorrection factor of 1.7; see text for details.

^bOn the assumption $g_1/g_0 = \frac{4}{3}$.

^c $\chi \equiv N^{-1}[\log(p_{\text{theor}}/p_{\text{expt}})]^2$, where N is the number of data points.

than the valence-band edge.

We next want to ascertain if the measured electrical-center concentrations for the two samples are indeed equal to their respective Cr concentrations. Secondary-ion mass spectroscopy (SIMS) measurements¹⁴ gave $[\text{Cr}] = 4 \times 10^{16} \text{ cm}^{-3}$ for 781/5, and $5 \times 10^{16} \text{ cm}^{-3}$ for 781/9. However, in an earlier comparison of SIMS results with neutron-activation (NA) results,¹⁵ on two unrelated Cr-doped GaAs samples of similar Cr concentrations, it was found that the SIMS results were lower by factors of 1.7, in both cases. Thus, if the same SIMS/NA relationship exists for the present samples, then their true Cr concentrations are $(6.8 \text{ and } 8.5) \times 10^{16} \text{ cm}^{-3}$, respectively, very close to the measured concentrations of the electrical centers. All other impurity concentrations measured by SIMS were more than a factor of 4 smaller than the Cr concentration. Thus, the relevant center cannot be associated with any impurity other than Cr, although at this stage, we cannot rule out a defect. Note also that the analytical results (SIMS and spark-source mass spectroscopy) show that the total shallow-acceptor

concentration (see Table I) cannot be due simply to Zn, even though the samples were doped (lightly) with Zn. Other impurities, and possibly defects, must be involved.

To prove that the electrical activation energy corresponds to the $\text{Cr}^{4+} - \text{Cr}^{3+}$ transition, we turn to some EPR measurements of Stauss *et al.*,³ in which they determined the Cr^{4+} , Cr^{3+} , and Cr^{2+} concentrations in several samples, of differing Fermi levels. Part of their Table I is reproduced as our Table II. From Eq. (3), after ignoring the terms involving $2\epsilon_F$, which turn out to be negligible for all samples listed in Table II (but not in general), we can write

$$\frac{N_{Cr}^{4+}}{N_{Cr}} = \frac{1}{1 + p^{-1}[(g_1/g_0)N_v \exp(-E_1/kT)]}, \quad (6a)$$

$$\frac{N_{Cr}^{2+}}{N_{Cr}} = \frac{1}{1 + p[(g_2/g_1)N_v \exp(-E_2/kT)]^{-1}}. \quad (6b)$$

At 295 K, Eq. (5) gives $E_1(4+ \rightarrow 3+) = 0.283 \pm 0.009 \text{ eV}$, and from some previous work,¹⁶ $E_2(3+ \rightarrow 2+) = 1.424 - 0.68 = 0.74 \text{ eV}$. The hole concentrations for the p -type samples of Stauss *et al.*³ can be

TABLE II. Concentrations of the various charge states of Cr in GaAs, at 295 K, as predicted by Eqs. (6a) and (6b), and as measured by EPR (Ref. 3). All concentrations in units of 10^{16} cm^{-3} .

Sample	ρ (295 K)	p (295 K)	[Cr]	[Cr ²⁺]		[Cr ³⁺]		[Cr ⁴⁺]	
	($\Omega \text{ cm}$)	(cm^{-3})	Meas.	Meas.	Pred.	Meas.	Pred.	Meas.	Pred.
1	0.074	$2.8 \times 10^{17} \text{ a}$	7.9	0	0	0	0	7.9	7.9
2A	224	$9.3 \times 10^{13} \text{ a}$	21.0	~ 0	0	16.7	11.6	4.3	6.9
2B	1950	$1.1 \times 10^{13} \text{ a}$	7.6	~ 0.1	0	7.2	7.1	≤ 0.3	0.4
3	5×10^8	$2.2 \times 10^{16} \text{ b}$	12.8	7.8	6.8	5	6.0	0	0
4	0.090	$3.9 \times 10^{-4} \text{ b}$	X^c	X	X	0	0	~ 0	0

^aEstimated from ρ with the assumption $\mu_p = 300 \text{ cm}^2/\text{V sec}$.

^bEstimated from ρ with the assumption $\mu_n = 4000 \text{ cm}^2/\text{V sec}$.

^cSimply stated as "observed" in Ref. 3.

estimated from their measured resistivities by assuming a hole mobility of $300 \text{ cm}^2/\text{V sec}$. For the SI and n -type samples, an electron mobility of $4000 \text{ cm}^2/\text{V sec}$ was assumed. These mobility estimates are not critical to the conclusions reached below.

The calculated Cr^{4+} , Cr^{3+} , and Cr^{2+} concentrations are presented along with the measured (EPR) concentrations in Table II. The agreement is quite remarkable, considering the various possible sources of error, and leaves no doubt that the measured electrical activation energy indeed corresponds to the $\text{Cr}^{4+} - \text{Cr}^{3+}$ transition. Note that the difference in temperature between the EPR measurements (4.2 K) and the electrical measurements (295 K) is unimportant here, because, in both cases, $p \ll |N_{DS} - N_{AS}|$, and thus, from Eq. (4), the $N_{\text{Cr}^{4+}}$ concentration should remain nearly the same from 4.2 to 295 K.

In summary, we have, for the first time, conclusively identified a transition which involves Cr^{4+} in GaAs namely the $\text{Cr}^{4+} - \text{Cr}^{3+}$ thermal transition. Room-temperature thermal energies, with respect to the valence band, can now be given for all three transitions: $E_1(4+ - 3+) = 0.28 \pm 0.01 \text{ eV}$; $E_2(3+ - 2+) = 0.74 \pm 0.02 \text{ eV}$; and $E_3(2+ - 1+) = 1.54 \pm 0.01 \text{ eV}$. By assuming that the recent photo-EPR^{2,3} and photoconductivity^{7,8} results pertain to the optical (absorption) $\text{Cr}^{4+} - \text{Cr}^{3+}$ transition, we can deduce a Franck-Condon shift of about 0.12 eV, at 150 K.⁷

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He-Scattering Investigation of CO Migration on Pt(111)

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The capability of a He-scattering experiment to detect the migration of adsorbed molecules on monocrystral surfaces is demonstrated for the first time. CO migration and island formation can be investigated at very low coverages because of the very large cross section for He scattering of CO adsorbed on Pt(111). The activation energy for CO migration on Pt(111) is found to be 7 kcal/mole. No island formation at low CO coverages on a defect-free Pt(111) surface was detected in the temperature range 120-400 K.

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A few years ago Schmidt stated that "measurements of surface diffusion rates on single-crystal planes are exceedingly difficult."¹ Reed and

Ehrlich noted in a recent paper² that, except for a number of field-emitter studies, the migration of adsorbed gases on single-crystal surfaces has