PHYSICAL REVIEW B VOLUME 16, NUMBER 3 1 AUGUST 1977

EPR of Cr^{2+} ($3d^4$) in gallium arsenide: Jahn-Teller distortion and photoinduced charge conversion*

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(Received 18 April 1977)

The spin-Hamiltonian parameters and low-temperature behavior of Cr^{2+} in GaAs are found to correspond closely to those in II-VI zinc-blende compounds, suggesting the occurrence of a static Jahn-Teller distortion. Observation of photoinduced charge conversion among Cr^{2+}, Cr^{3+}, and Cr^{1+}, each possessing a different local symmetry, offers independent evidence that the lowered symmetries at the Cr^{2+} and Cr^{3+} sites are Jahn-Teller generated.

In this paper, we report the EPR identification of a tetragonal Jahn-Teller distorted Cr^{2+} ($3d^4$) center in Cr-doped GaAs and the photosensitivity of the EPR signal to infrared radiation with photon energy $h\nu$ less than E_g, the band gap. When this finding is taken together with recent work on the Cr^{3+} ($3d^3$) center[1] and the Cr^{1+} ($3d^5$) center[2] in GaAs:Cr, the very unusual properties of Cr in GaAs become evident. These include (i) the existence of three distinct charge states identifiable by EPR, (ii) the apparent existence of static Jahn-Teller effects in two of these charge states at sufficiently low temperatures, and (iii) photoinduced interconversion between the charge states with $h\nu < E_g$. To our knowledge no other transition-metal dopant has been found to exhibit so wide a variety of behavior in a semiconductor host.

GaAs has the zinc-blende structure. Our experimental results imply that the Cr ion is tetrahedrally coordinated by As and we assume that Cr is substitutional for Ga and not located in the interstitial site which has As nearest neighbors. Since the $3d^3$ and $3d^4$ ground manifolds are orbitally degenerate in tetrahedral symmetry, they may exhibit static or dynamic Jahn-Teller effects at sufficiently low temperatures.[3] On the other hand, the orbital singlet $3d^5$ ion is not Jahn-Teller sensitive and hence should accurately reflect the symmetry of the Cr^{1+} surroundings in the absence of a spontaneous distortion. Thus, if it is possible to convert the charge state of a given Cr ion from 3+ or 2+ to 1+, one can determine whether the Cr ion is associated with a nearby impurity or defect. Experimentally, the Cr^{1+} site symmetry is accurately cubic,[2] implying that there is no localized defect associated with the Cr^{1+} ion.

The low-lying states of Cr^{2+} in a variety of II-VI compounds with the zinc-blende structure have been discussed in considerable detail by Vallin and Watkins.[4] Drawing on EPR, near- and far-infrared optical absorption, and EPR stress effect measurements, they concluded that in each case the tetrahedrally coordinated Cr^{2+} undergoes a static tetragonal Jahn-Teller distortion reducing the symmetry to D_{2d}. This distortion lifts the degeneracy of the $^5T_2$ ground state leaving an orbital singlet $^5B_2$ lowest with spin $S = 2$.

Our experimental data were obtained with a Varian E-9 X-band EPR spectrometer equipped with an optical port and a variable-temperature insert. The angular dependence of the Cr^{2+} EPR signals in the $(1\bar{1}0)$ plane of GaAs at 5 K is shown in Fig. 1. This is just the spectrum expected for such an

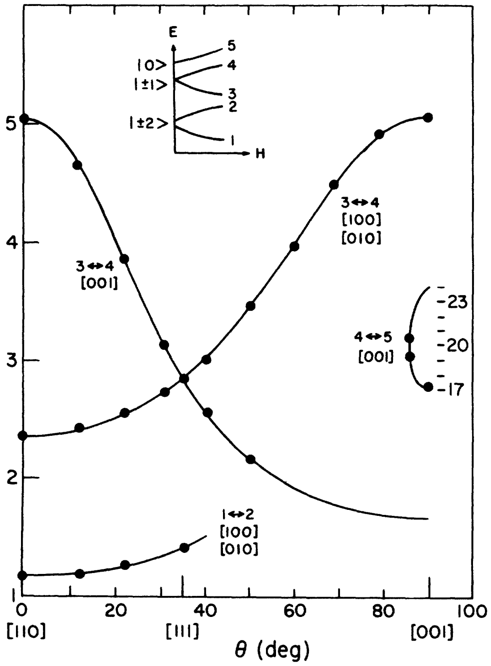

FIG. 1. Observed (●) and computed angular dependence of X-band Cr^{2+} EPR signals at 5 K for H in the $(1\bar{1}0)$ plane of GaAs. Transitions are labeled via the energy levels shown in the inset and by their distortion axes. Note that the high-field 4 ⟷ 5 transition has its own magnetic field scale.

TABLE I. EPR parameters of Cr centers in GaAs at 5 K.

Center	g values	a(cm^{-1})	D(cm^{-1})	E/D	Ref.
Cr^{1+}	1.993, 1.995(1)	<0.0006	···	···	Ref. 2 and this work
Cr^{2+}	$\parallel$ 1.974(3) $\perp$ 1.997(2)	+0.031(13)	−1.860(16)[a]	0	This work
Cr^{3+}	⟨100⟩ 5.154(2)[b] ⟨011⟩ 2.367(1) ⟨01$\bar{1}$⟩ 1.636(1)	···	3.2(9)	0.265(1)	Ref. 1

[a] Assumes $F=0$ (see text). We find that $D-a-\frac{2}{3}F=-1.891(3)$ cm^{-1}.

[b] Effective g values for ground doublet.

$S=2$ center with roughly equal numbers having tetragonal distortions along the three different ⟨100⟩ directions.[4] Additional data taken in the (100) plane show that the distortion is purely tetragonal. The various EPR transitions observed are identified in Fig. 1 in terms both of their distortion axes z and of the energy levels shown schematically in the inset. In the experimental setup used for Fig. 1, the microwave field $\vec{H}_1 \parallel [1\bar{1}0]$ so that the $3 \leftrightarrow 4$ transition is forbidden for $\vec{H} \parallel \vec{z}$ and the $1 \leftrightarrow 2$ transition is forbidden for $\vec{H} \perp \vec{z}$ or $\vec{H}_1 \perp \vec{z}$. These selection rules are reflected in the disappearance of those resonances in parts of the angular range.

The EPR spectra of all three Cr ions can be described in terms of the general spin Hamiltonian

$$\mathcal{H} = \mu_B \vec{S}\cdot\vec{g}\cdot\vec{H} + DS_z^2 + E(S_x^2 - S_y^2) + \tfrac{1}{6}a(S_x^4 + S_y^4 + S_z^4) + \tfrac{1}{180}F\{35S_z^4 + [25 - 30S(S+1)]S_z^2\}.$$

The parameters required to fit the Cr^{2+} data are shown in Table I, and the solid lines in Fig. 1 are calculated using these parameters and exact diagonalization of the spin Hamiltonian. The actual values of the parameters were determined by computer analysis of the accurately measured line positions for H parallel to [001], [110], and [111]. The data are relatively insensitive to the value of the cubic field a parameter because of its small size, and intensity information from the $1 \leftrightarrow 2$ line (proportional to a^2) was used in adopting the best value. The sign of D was determined from the temperature dependence of the $3 \leftrightarrow 4$ and $4 \leftrightarrow 5$ EPR lines for $\vec{H} \parallel [001]$. (Actually $D - \frac{2}{3}F$ rather than D is the quantity determined but we take[4] $F \simeq 0$.)

Above about 12 K the Cr^{2+} EPR lines in GaAs begin to broaden rapidly and can no longer be seen above 20 K. Simultaneously the line shape changes from nearly Gaussian to nearly Lorentzian. This behavior is analogous to that exhibited by Cr^{2+} in the II-VI compounds.[4] As was found earlier for the GaAs Cr^{3+} center,[1] stress associated with mounting the sample affects the relative signal strength from differently oriented Cr^{2+} centers. Thus, the available data indicate that Cr^{2+} has the same characteristics, including the order of magnitude of the axial-distortion parameter D, in GaAs as in the II-VI zinc-blende compounds. This strongly suggests that the observed tetragonal distortion in GaAs is Jahn-Teller generated.

In Table I we give also the spin-Hamiltonian parameters appropriate to the Cr^{3+} and Cr^{1+} centers. The Cr^{3+} $S=\frac{3}{2}$ spectrum, which decreases in intensity very rapidly with temperature, is unobservable for $T>10$ K. Its reduction in symmetry to C_{2v} has already been attributed[1] to a static Jahn-Teller distortion. The isotropic Cr^{1+} signal, observed only after photoexcitation of Cr-doped samples, follows a T^{-1} temperature dependence. Our own data support the assignment[2] of this signal to $S=\frac{5}{2}$ Cr^{1+} in T_d symmetry; the negative g-shift, although unusually large, and the small cubic-field splitting implied by the isotropic linewidth are in accord with the behavior of Cr^{1+} in other materials.[5]

Illuminating the sample with monochromatic light having $h\nu < E_g$ can alter significantly the intensity of the Cr^{2+} EPR signal as well as those[1,2] of Cr^{3+} and Cr^{1+}. Because of trapping effects,[6] the observed changes in Cr^{2+} signal strength for an initial scan through the energy range 0.5–1.6 eV are different from those for subsequent scans. The changes are also dependent on the direction of the initial scan. After one scan, however, the variation in EPR signal strength with $h\nu$ is essentially independent of scan direction and we refer to this as the reversible photoinduced effect. This effect for Cr^{2+} is shown by the data points in Fig. 2 where the ordinate is the light-on EPR signal height. Also shown by solid lines in Fig. 2 are the reversible photoinduced values of the Cr^{1+} signal in the same sample and of the Cr^{3+} signal in a more strongly doped GaAs : Cr sample (required for good Cr^{3+} signal-to-noise ratio). Note that the base line for the Cr^{3+} has been suppressed to emphasize the shape of the curve.

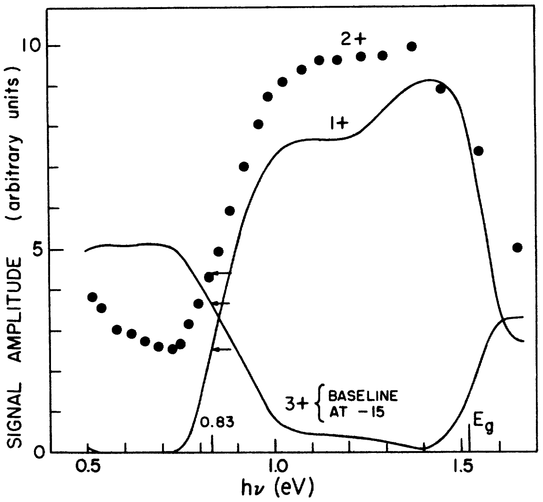

FIG. 2. "Reversible" effect of monochromatic infrared illumination on the EPR signal amplitudes of $Cr^{1,2,3+}$ in GaAs at 5 K. Note the suppressed zero for Cr^{3+}. Illumination at 0.83 eV has no effect (see text) and the corresponding dark-signal values are indicated by arrows.

When the monochromatic light is switched off, each of the EPR signals returns to a steady-state dark value in a time ranging from several seconds to several minutes depending on the wavelength used. At $h\nu \simeq 0.83$ eV illumination produces *no change* in any of the signals from this dark value. For $h\nu < 0.83$ eV, however, the Cr^{3+} signal increases in magnitude while the Cr^{2+} and Cr^{1+} signals decrease when the light is switched on. For $h\nu$ between 0.83 eV and E_g this situation is reversed as Fig. 2 illustrates. For $h\nu > E_g$, the observed fall-off in photoresponse is due to the strongly absorbed light stimulating only a thin surface layer. It is interesting that for $h\nu < 0.73$ eV the Cr^{1+} signal can be completely eliminated.

Independent of the details[7] of the transitions which induce these effects, the observed changes indicate that monochromatic light converts Cr^{3+} to $Cr^{2+} + Cr^{1+}$ for $h\nu > 0.83$ eV, while the conversion is in the opposite sense for $h\nu < 0.83$ eV. Since the symmetries of the three states of Cr are different and neither tetragonal nor cubic symmetry is compatible with a single associated defect, the photoinduced interconversion by itself offers persuasive evidence that the lowered symmetries of the 2+ and 3+ charge states are due to spontaneous distortions, i.e., to static Jahn-Teller effects.

The EPR data directly indicate that, at least at 5 K, it is possible to have Cr in three charge states simultaneously in a suitably (optically) prepared GaAs sample. Both Cr^{3+} and Cr^{2+} act as electron traps so that Cr is a double acceptor in GaAs. At low temperatures, Cr^{1+} slowly reconverts to Cr^{2+}.

The results described above can be important to the analysis of the Cr-doped semi-insulating GaAs used for microwave devices since the concentration of Cr in the 1+ and 2+ charge states can be determined from the intensities of the corresponding EPR lines at liquid-helium temperatures. Using the parameters in Table I to calculate the necessary transition probabilities and thermal populations, we have found that concentrations down to 10^{14} cm^{-3} can be measured reliably. For Cr^{3+}, however, the strong dependence of the observed signal on temperature and stress[1] makes such an approach less reliable.

Since Cr^{2+} exhibits a static Jahn-Teller effect in GaAs, one might expect to see similar Cr^{2+} behavior in other III-V compounds. We have, in fact, observed such behavior in Cr-doped InP.[8]

The authors wish to thank Professor R. H. Bube and E. M. Swiggard for the crystals they supplied.

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*Supported in part by the Office of Naval Research.

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