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EPR of Cr($3d^3$) in GaAs—evidence for strong Jahn-Teller effects

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The X-band EPR spectrum of $\mathrm{Cr}^{3+}(3d^3)$ has been observed in semi-insulating Cr-doped GaAs at 5 K. The Cr is assumed to be substitutional for Ga. The $S = 3/2$ center has an orthorhombic (C_{2v}) symmetry spin Hamiltonian $\mathcal{H} = \mu_B \sum_i g_i H_i S_i + D[S_z^2 - S(S+1)/3] + E(S_x^2 - S_y^2)$ with x, y, z being [110], [001], [$1\bar{1}0$] respectively. The zero-field splitting $2(D^2 + 3E^2)^{1/2} = 7 \pm 2\ \mathrm{cm}^{-1}$ while $E/D = 0.26$. Most of the lines observed arise from the ground doublet which can be characterized by a simple $S' = 1/2$ spin Hamiltonian with $g_x' = 2.367$, $g_y' = 5.154$, and $g_z' = 1.636$. The relative and absolute intensities of the six crystallographically equivalent centers are sensitive to applied stress and upon warming the lines broaden and disappear above 10 K. The spectrum is thought to arise from a strongly Jahn-Teller–distorted Cr center which reorients rapidly above 5 K. The effect of illumination with $h\nu$ less than the band gap has also been measured.

I. INTRODUCTION

Chromium is the common dopant used to produce semi-insulating ($\rho > 10^8\ \Omega\,\mathrm{cm}$) GaAs for device substrates. It acts as a deep acceptor and compensates the shallow donors which are always present in bulk-grown GaAs. The importance of Cr in this context has stimulated a number of investigations to locate the Cr energy levels in the forbidden gap.[1-4] Although there is some disagreement, in general $E_c - E(\mathrm{Cr}) = 0.80 \pm 0.03$ eV has been established for the filled acceptor level.[5] Recent acoustic-paramagnetic-resonance[6] and especially low-temperature optical-absorption[3] experiments have indicated that the acceptor can be considered to be $\mathrm{Cr}^{2+}(3d^4)$ when the acceptor level is filled.[7]

If the Cr concentration is greater than that of the shallow donors, $\mathrm{Cr}^{3+}(3d^3)$ will be present also. Since this is a Kramers ion, one would expect to observe electron paramagnetic resonance (EPR) at sufficiently low temperatures. However, previous attempts[1,6,8] have detected no EPR signal which could be attributed to either Cr^{3+} or Cr^{2+}. Because substitutional $3d^3$ ions in GaAs have orbitally degenerate ground states, they are unstable to Jahn-Teller distortions. In this paper we show that one can observe the EPR of Cr^{3+} in GaAs and that the characteristics of the observed spectrum are most easily interpreted in terms of a strong Jahn-Teller effect.

II. CRYSTAL-FIELD MODEL OF Cr CENTER

We assume that Cr replaces Ga in the GaAs structure. Chromium can exist in either the Cr^{3+} or Cr^{2+} valence state depending on whether the chromium acceptor[9] is neutral or negatively charged. Here we consider only the neutral Cr^{3+} acceptor. This is the predominant state of Cr if the chromium concentration significantly exceeds the concentration of shallow donors in the crystal.

In Fig. 1, we show the lower-lying energy levels of the $3d^3$ ion Cr^{3+}. The free-ion levels split as illustrated under the action of the cubic field with tetrahedral symmetry. Because we observe orthorhombic (consistent with C_{2v}) symmetry in this work, we invoke a lower-symmetry crystal field of the form $V_c = Al_z^2 + B(l_x^2 - l_y^2)$ with $A > B > 0$ which splits the ground ${}^4T_1$ manifold as shown. This results in three orbital singlets each with fourfold spin degeneracy.

As Henning *et al.*[10] have shown, if $A - B \gg \lambda$, the spin-orbit parameter, then the ground orbital singlet can be described by a spin Hamiltonian of the form

$$\mathcal{H} = \mu_B \sum_i g_i H_i S_i + D[S_z^2 - \tfrac{1}{3}S(S+1)] + E(S_x^2 - S_y^2) , \tag{1}$$

with the following approximate expressions for the parameters:

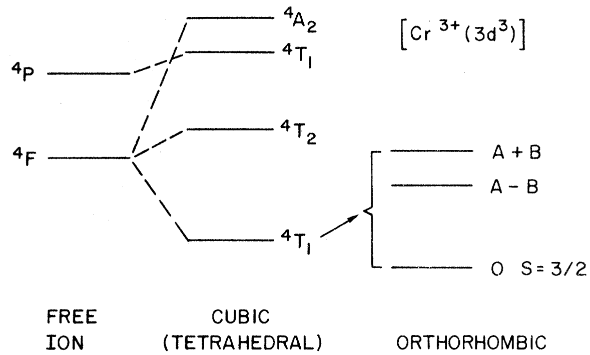

FIG. 1. Splitting of the lowest-lying Cr^{3+} ($3d^3$) states under the action of tetrahedral and orthorhombic $[Al_z^2 + B(l_x^2 - l_y^2)]$ crystal fields neglecting spin-orbit effects.

$$\begin{aligned} g_x &= g_e - 2\gamma^2\lambda/(A+B)\ , \quad D = A\gamma^2\lambda^2/(A^2 - B^2)\ ,\\ g_y &= g_e - 2\gamma^2\lambda/(A-B)\ , \quad E = (B/A)D\ , \qquad (2)\\ g_z &= g_e\ . \end{aligned}$$

Here g_e is the free-electron g value, and γ, which depends on the admixture of ^4P into the $^4T_1$ ground manifold, obeys the relation $-\frac{3}{2} \le \gamma \le -1$.

The effect of the zero-field terms D and E is to split the $S=\frac{3}{2}$ state into two doublets separated by $2Q \equiv 2(D^2 + 3E^2)^{1/2}$. If the ground-state splitting is large enough that the microwave quantum $h\nu \ll 2Q$, then it is possible to treat both the ground and excited doublets as effective spin $S' = \frac{1}{2}$ states with simple $\mathcal{H} = \mu_B \vec{H} \cdot \overleftrightarrow{g}' \cdot \vec{S}'$ Hamiltonians. For the ground doublet the g' values are related to the $S = \frac{3}{2}$ parameters by[10]

$$\begin{aligned} g'_x &= g_x[1 + (D - 3E)/Q]\ ,\\ g'_y &= g_y[1 + (D + 3E)/Q]\ , \qquad (3)\\ g'_z &= g_z(2D/Q - 1)\ . \end{aligned}$$

It is easy to show that the upper doublet g' values can be obtained by replacing D and E by their negatives in Eqs. (3) and taking the absolute g' values. Under the condition $h\nu \ll 2Q$, none of the otherwise allowed transitions between the two doublets will be observed.

III. APPARATUS AND SAMPLES

The samples used in this work are single crystals of Cr-doped GaAs, either obtained from Monsanto or grown in our laboratory.[11] A typical sample has dimensions $1 \times 3 \times 12$ mm^3. They were x-ray aligned and cut with long axes along either $[1\bar{1}0]$ or $[11\bar{2}]$. Since spark spectroscopy could not differentiate adequately among the samples for the small Cr concentrations present, relative Cr concentrations were obtained from mass spectroscopic analysis and 0.8-eV photoluminescence.[5] We label the samples 1, 2, 3; on the basis of the above analyses, their relative Cr concentrations are about 9:2:1. The Cr concentration in sample 1 is estimated to be a few parts per million.

The EPR spectra were taken with a Varian E-9 spectrometer at 9.15 GHz. The temperature of the sample was varied using a Helitran Model LTD-3-110 cryogenic cooler which bathes the sample in a stream of cold He gas. Sample temperatures were measured using a calibrated Au(Fe)-chromel thermocouple located in the gas stream approximately 1 cm before the sample. The samples were also illuminated with monochromatic light while the EPR spectrum was monitored. The output of a monochromator covering the photon energy range 0.5–1.6 eV was filtered with silicon or germanium to remove higher orders and focused on the sample through slits in the microwave cavity.

IV. EXPERIMENTAL RESULTS

Typical EPR spectra from sample 1 at 5.0 K are shown in Fig. 2, for $\vec{H} \parallel [110]$ and $\vec{H} \parallel [001]$. These data were taken with the microwave field $\vec{H}_1 \parallel [1\bar{1}0]$. The observed EPR lines in Fig. 2 arise from two distinct centers which we label A and B. The A center is identified as Cr^{3+} as indicated below. The B center is actually Cr^{2+}; details will be published later. The angular dependence of the A spectrum lines is shown by the experimental points in Figs. 3 and 4 for $\vec{H}$ rotating in $(1\bar{1}0)$ and $(11\bar{2})$ planes, respectively. For the [110] and [001] orientations of $\vec{H}$, accurate line positions were measured with an NMR magnetometer and are shown in Table I. Typical linewidths for the A spectrum at 5.0 K are in the range 120–250 G, which we attribute largely to unresolved hyperfine splittings by both Ga and As nuclei. As a result, nearby lines in the spectrum frequently are merged and the resulting imprecision in line positions is reflected in the data of Figs. 3 and 4.

Sample 1 was the only GaAs:Cr sample which allowed quantitative determination of the A spectrum line positions and intensities. Sample 2 showed a much weaker A spectrum and sample 3 showed no usable A spectrum. These results are consistent with the observed relative Cr concentrations.

When the sample temperature is raised above 5.0 K there is an extremely rapid decrease in the observability of the A spectrum lines. This is shown graphically in Fig. 5 for $\vec{H} \parallel [201]$. Above 10 K the A spectrum is too weak to be observed. Careful checks and the markedly different behavior of the B center lines in Fig. 5 show that this is not an experimental artifact. Temperatures up to 30 K were used in an attempt to observe some new spectrum which might arise from motional averaging of the A spectrum, but none was found. It is clear from the data that the transitions are being broadened by either relaxation or motional averaging effects as the temperature is increased. However, subject to considerable limitation due to poor signal to noise, it is also apparent that the observable broadening does not account for all of the reduction in intensity.

The samples used in these experiments were mounted on a quartz rod using rubber cement. The cleavage fracture of several samples made it clear that this method of mounting results in considerable stress on the sample as it is cooled rapidly from room temperature to the liquid-helium range. When the samples are mounted in a stress-free

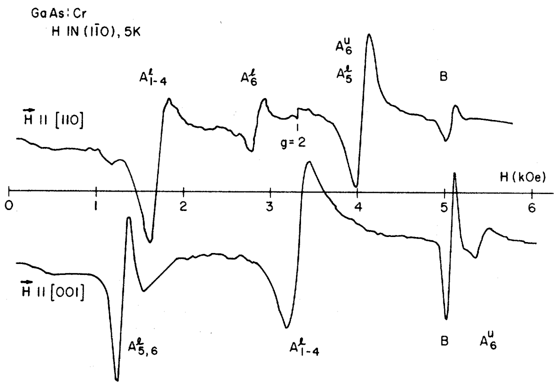

FIG. 2. Representative EPR spectra of GaAs:Cr^{3+}. The labels are explained in the text.

manner, the observed A spectrum signals are much weaker, as is also the case when stress is relieved by fracture. Furthermore, the *relative* intensities of the various A lines depend on whether the sample is stressed or not. Unfortunately, the nature of the applied stress is complex and future experiments with controlled uniaxial stress are planned to investigate this effect in detail.

The intensity of the A spectrum can be altered by illuminating the sample with monochromatic light having a photon energy $h\nu$ less than the band gap (~1.5 eV). The effect of such illumination is shown in Fig. 6. As can be seen, the fractional changes in intensity are fairly small (±10%). Furthermore, the effect is time and history dependent. The steady-state light-on values in Fig. 6 depend somewhat on whether $h\nu$ is being stepped in an increasing or decreasing sense through the 0.5–1.6-eV range. After an initial light scan in either direction, the effect becomes reversible.

We will not attempt to explain the details of the photostimulated changes at this time, but it should be noted that there are three broad regions in Fig. 6: one in which the A signal increases when the

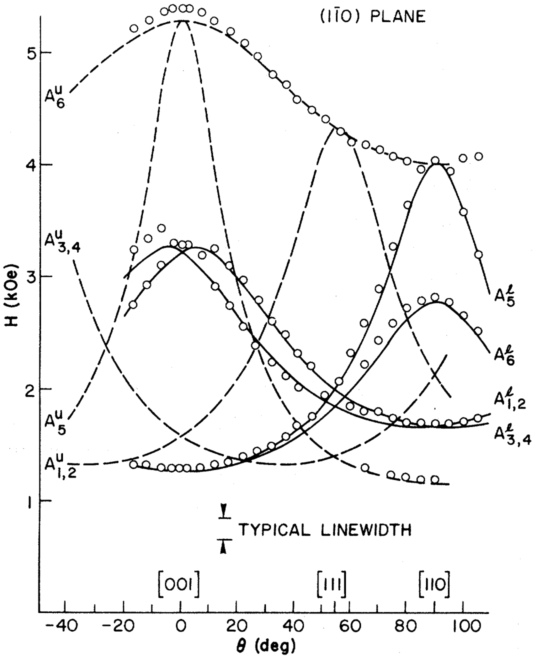

FIG. 3. Angular dependence of GaAs:Cr^{3+} EPR in the (1$\bar{1}$0) plane. The solid lines are theoretical fits to the experimental points (○). See text for labeling.

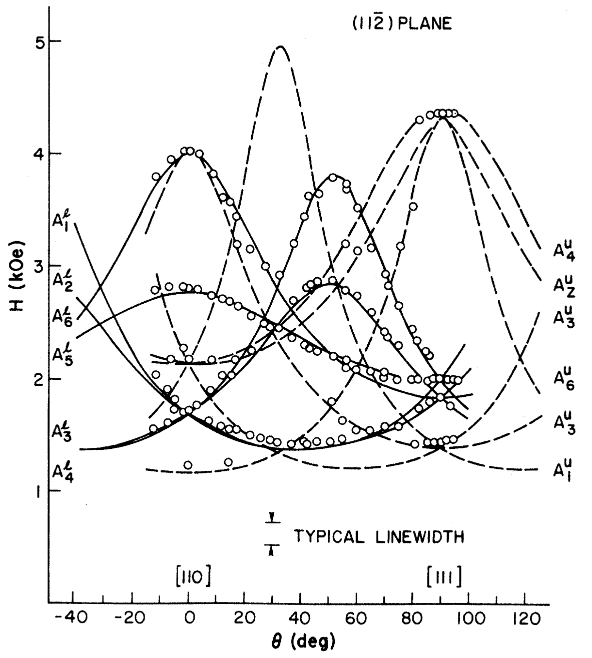

FIG. 4. Angular dependence of GaAs:Cr^{3+} EPR in the (11$\bar{2}$) plane. The solid lines are theoretical fits to the experimental points (○). See text for labeling.

TABLE I. Line positions and lower doublet g' values ($S'=\frac{1}{2}$). $Cr^{3+}(3d^3)$ EPR in GaAs.

EPR line[a]	H (G)[b]	g'_i[c]
$\vec{H}\parallel[110]$		
A^l_{1-4}	1668	
A^l_6	2764	2.367(1)[110]
A^l_5	3998	1.636(1)[1$\bar{1}$0]
$\vec{H}\parallel[001]$		
$A^l_{5,6}$	1269	5.154(2)[001]
A^l_{1-4}	3255	...
A^{μ}_6	5392	...

[a] See Fig. 2 for EPR line designations.
[b] Microwave frequency 9.1550 GHz.
[c] Directions of principal g' values are shown.

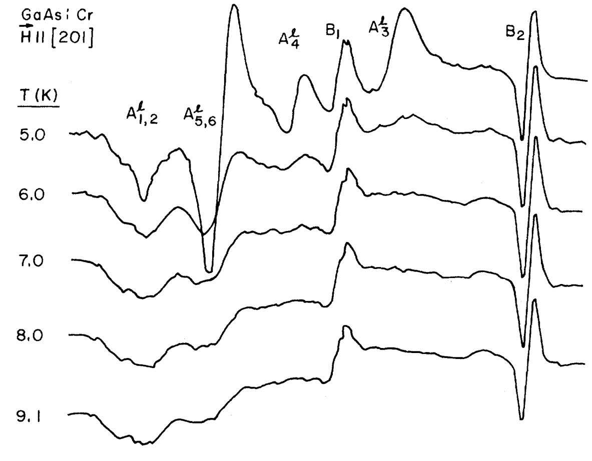

FIG. 5. Temperature dependence of A (Cr^{3+}) and B EPR spectra.

light is on; one in which it decreases; and the one with $h\nu > 1.5$ eV in which light has little effect. For $h\nu > 1.5$ eV, only a very thin surface region is directly affected by the light because of the very large absorption coefficient so that the majority of the Cr^{3+} centers sampled by EPR are left unmodified. This lack of change shows that the photoeffects which are observed are not due to sample warming. For $h\nu > 0.75$ eV it is known from photoconductivity and photo-Hall measurements[4] that electron-hole pairs are created in Cr-doped GaAs via intermediate states in the band gap. The decrease in Cr^{3+} signal in the 0.85-1.5-eV range is therefore attributed to the conversion of Cr^{3+} to Cr^{2+} by capture of valence-band electrons. The mechanism for the increase in Cr^{3+} signal for $h\nu < 0.85$ eV is not clear.

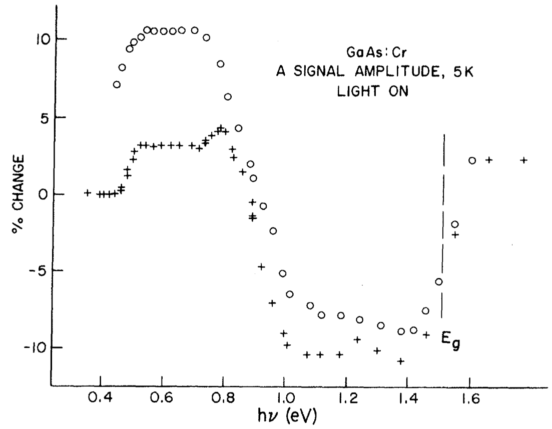

FIG. 6. Spectral dependence of the light-induced changes in Cr^{3+} EPR signal. Changes are measured with respect to the cooled-in-dark condition. Note the dependence on the direction in which the photon energy is changed. (+), initial low-to-high energy scan; (O), subsequent return. Data below 0.5 eV are not valid.

V. DISCUSSION

A. Comparison with crystal-field model

We first consider the EPR lines labeled A_i^{ℓ} in Figs. 3 and 4. From their number, their degeneracies along high-symmetry directions, and their angular dependence, one can conclude that they arise from six crystallographically equivalent centers. Each center is characterized by an $S' = \frac{1}{2}$ spin Hamiltonian with orthorhombic (C_{2v}) symmetry and with principal g' values along $x = [110]$, $y = [001]$, and $z = [1\bar{1}0]$ or equivalent sets of (x, y, z).[12] The principal g' values were determined from the data in Table I and are given in Table I. Using these values, the theoretically predicted positions of the EPR transitions of all six centers are indicated by the solid lines in Figs. 3 and 4. The results clearly verify the orthorhombic $S' = \frac{1}{2}$ Hamiltonian.

We now compare this spectrum with that arising from the ground doublet of Cr^{3+} in a distorted tetrahedral site in line with the model discussed earlier. Using Eqs. (3), the g' values of Table I then imply that the $S = \frac{3}{2}$ system can be characterized by $g_x = 1.998$, $g_y = 1.958$, and $E/D = 0.266$, where we have taken $g_z = 2.0023$. Furthermore, one can get an estimate of D from the approximate expression[10]

$$2D \simeq \lambda[g_e - \tfrac{1}{2}(g_x + g_y)] , \tag{4}$$

which yields $D \simeq 1.1$ cm^{-1} or $2Q \simeq 2.4$ cm^{-1} for the ground-state splitting using[13] $\lambda = 90$ cm^{-1} for Cr^{3+}. While this is not an accurate estimate it does indicate that $h\nu \ll 2Q$ as required for the validity of Eq. (3).

More important, however, this result indicates that the excited doublet should be populated at 5 K and that one should be able to see transitions within this doublet. No new parameters are required to calculate the line positions within the $h\nu \ll 2Q$ approximation and the predicted EPR line positions for the six excited doublets are shown as dashed curves in Figs. 3 and 4 labeled A_i^u. The data near the A_6^u curve in Fig. 3 clearly arise from the upper doublet and, near high-symmetry directions, data associated with other A_i^u curves can be seen. In this connection it should be noted that the theoretical EPR line intensities are in general strongly dependent on the orientation of both $\vec{H}$ and the microwave field $\vec{H}_1$ with respect to the principal axes because of the strong g anisotropy in both the ground and excited doublets.[14] Explicit calculations show that for $\vec{H}_1 \parallel [1\bar{1}0]$ as in Fig. 3, the EPR line A_6^u is by far the most intense upper doublet line and that its intensity is independent of the orientation of $\vec{H}$ in $(1\bar{1}0)$. This agrees with our findings. Thus, taken in conjunction with the correlation between the A spectrum intensity and the Cr concentration, the above results offer strong evidence that the entire A spectrum arises from an orthorhombically distorted tetrahedrally coordinated Cr^{3+} center.

We now attempt to improve our estimate of the ground-state splitting. There are at least two methods for doing this. The first is to calculate the higher-order Zeeman perturbations which couple the upper and lower doublets and then to calculate the $2Q$ value needed to improve the fit. The second involves comparing the relative experimental and theoretical intensities of A_i^l and A_i^u lines arising from the same center and evaluating $2Q$ from the population ratio deduced.

Explicit calculations show that the second-order Zeeman terms do not shift the apparent EPR line positions and hence one must go to third order to get a result. The A_6^u line position for $\vec{H} \parallel [001]$ is the most sensitive to this perturbation. When one improves the fit for this line, the parameters given earlier are found to change to $E/D = 0.263$, $g_x = 1.985$, and $g_y = 1.962$, together with $2Q \simeq 5.4$ cm^{-1}. This $2Q$ value is not fully consistent with the A_6^u line position for $\vec{H} \parallel [110]$ which suggests a larger $2Q$ value, although accurate quantitative calculation is difficult because of A_6^u and A_5^l overlap in that orientation. The best estimate of $2Q$ from population effects can be obtained from the intensities of the A_6^u and A_6^l lines in Fig. 3. This gives $\exp(-2Q/kT) = 0.05$ at 5.0 K, or $2Q = 10.4 \pm 1.5$ cm^{-1}. Taking all the data into account we estimate $2Q \simeq 7 \pm 2$ cm^{-1}, showing that Eq. (4) underestimates the true value.

B. Orthorhombic distortion

We now consider possible origins for the distortion observed for the Cr^{3+} center. The simplest possibility is to assume that there is another defect associated with the Cr^{3+} ion. An alternative possibility is a Jahn-Teller distortion. Both models are illustrated in Fig. 7.

1. Associated defect

To be consistent with the observed symmetry, an associated defect would have to be located along a ⟨100⟩-type direction. If the Cr is in a Ga site, the nearest sites would be the nearest-neighbor interstitial site $\frac{1}{2}a$ away and the next-nearest-neighbor Ga site at distance a. The fact that the A center can be reoriented by stress below 300 K rules out the substitutional location on the basis of migrational energy considerations. However, such a reorientation under stress (as well as the possible formation of new Cr-defect pairs) during cooldown from room temperature does not put unreasonable constraints on the migrational energy barrier for interstitial defects, since rates of 10^{-2} sec^{-1} at 100 K would be adequate (i.e., $E_{\text{migr}} \leq 0.3$ eV). The interstitial defect could be charged or neutral. However, if it were charged, one would expect the D-term distortion axis of the center to be along ⟨001⟩, whereas we find it to be along ⟨110⟩. Hence a neutral defect in the nearest interstitial site is the more likely associated defect. This is consistent with the fact that Cr^{3+} at a Ga site requires no charge compensation.

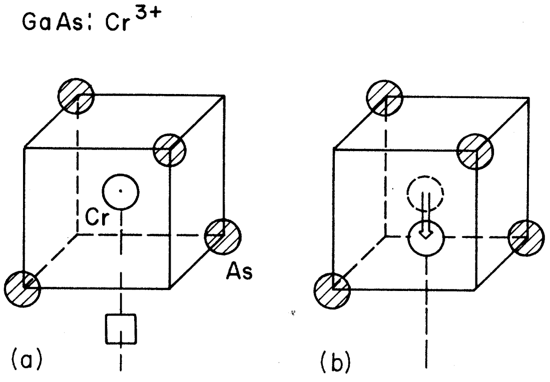

FIG. 7. Possible models of the GaAs:Cr^{3+} center: (a) associated defect model; (b) Jahn-Teller distortion model. The Cr displacement is along ⟨100⟩.

How can one explain the dramatic disappearance of the A center signal as T increases from 5 to 9 K? The possibilities are (i) broadening due to motion of the associated defect from one interstitial site to another via the "channels" in the zincblende structure or (ii) spin-lattice relaxation broadening. The first of these would require a jump rate of ~10^9 sec^{-1} at 6 K. If one assumes $\nu = 10^{14} \exp(-\Delta/T)$ as the jump frequency, then $\Delta \simeq 70$ K (0.006 eV). This is an unacceptably low value for the barrier between two adjacent interstitial sites. On the other hand, if spin-lattice broadening is invoked, we are then faced with the requirement that $T_1^{-1} \simeq 10^9$ sec^{-1} at 6 K. Since Cr^{3+} in a distorted site has an orbital singlet ground state, one would expect[14] to find $T_1^{-1} \leq 10^6$ sec^{-1} with no consequent line broadening.

Thus while an associated neutral defect in the nearest interstitial site has many of the required properties, such a model is not able to explain the rapid loss of EPR signal above 5 K.

2. Jahn-Teller distortion

It should be noted at the outset that the symmetry of the observed orthorhombic distortion is not consistent[15] with the usual treatment of the Jahn-Teller effect. However, there are known to exist a class of centers reviewed both by Sturge[16] and by Ham[17] which exhibit Jahn-Teller distortions with large stabilization energies. At low temperatures they exhibit a spontaneous static distortion with several energetically equivalent orientations and reorient between these configurations at a thermally activated rate as the temperature is increased. Many of them also reorient under stress and several exhibit an orthorhombic symmetry of the type found here. Perhaps the most notable among these for our purposes are the EPR centers due to Ni$^-$ in Ge[18] and Pd$^-$ and Pt$^-$ in Si.[19] Each of these three cases has tetrahedral coordination and shows an $S=\frac{1}{2}$ spectrum with principal axes [110], [1$\bar{1}$0], and [001]. Furthermore, Ni$^-$, Pd$^-$, and Pt$^-$ act as deep acceptors in their respective hosts just as does Cr^{3+} in GaAs.

It is clear that the characteristics exhibited by the Cr^{3+} center in GaAs are essentially the same as the above class of Jahn-Teller centers in Ge and Si. One can get an estimate of the splitting of the ground ${}^4T_1$ manifold from g_y and Eq. (2). Using $\lambda = 90$ cm^{-1} gives $A \simeq 5600$ cm^{-1}, where we have taken $\gamma = -\frac{3}{2}$ and allowed for equal spin-orbit and orbital reduction factors $K_{so} = K_L = \frac{2}{3}$. Thus, the ${}^4T_1$ splitting $(A+B)$ is probably larger than the ${}^4T_2 - {}^4T_1$ cubic field splitting (Fig. 1), which means that one definitely would be in the very strong Jahn-Teller-effect regime.[16,17] Furthermore, the components of ${}^4T_1$ and ${}^4T_2$ in Fig. 1 would become strongly admixed so that Eq. (2) can have only qualitative validity.

Taking all the evidence into account, we believe that the orthorhombic distortion of the Cr^{3+} center in GaAs arises from a strong Jahn-Teller effect and that the disappearance of the spectrum for $T > 10$ K is due to rapid reorientation which broadens the EPR lines sufficiently to make them unobservable. Before the regime of motional narrowing is reached, the spectrum has become too weak to observe either because of strong spin-lattice relaxation or simply from loss of signal intensity due to the increased temperature.

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