EPR study of Fe^{3+} and Cr^{2+} in InP†

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At 4.5 K, Fe^{3+} ($3d^5$) displays a cubic-symmetry EPR spectrum in InP similar to that in related III-V semiconductors, with parameters $g = 2.0235(10)$ and $a = +221(2) \times 10^{-4}$ cm^{-1}. Optical transitions near 0.75 and 1.13 eV produce transient decreases in the Fe^{3+} signal. The Cr^{2+} ($3d^4$) site symmetry in InP is reduced to tetragonal (D_{2d}) by a Jahn-Teller distortion as in GaAs. The Cr^{2+} EPR parameters found are $g_{\parallel} = 1.981(3)$, $g_{\perp} = 2.010(5)$, $D - a - 2F/3 = -1.056(1)$ cm^{-1}, $|a| = 0.089(7)$ cm^{-1}.

I. INTRODUCTION

There is current interest in both iron and chromium doping of InP to produce semi-insulating microwave device substrates.[1] As a result, it is desirable to be able to determine the valence states and concentrations of Fe and Cr in InP at the ppm level or lower. To that end, in this paper we report on the detection of the low-temperature EPR spectra of both Fe^{3+} and Cr^{2+} in InP. In addition, we show that the Fe^{3+} signal intensity is sensitive to infrared light and that the symmetry of the Cr^{2+} center is lowered by a static Jahn-Teller effect.

The samples used in this work were grown by the liquid-encapsulated Czochralski technique and the transition-metal ion concentrations were determined by comparing the EPR intensities with a National Bureau of Standards Al$_2$O$_3$:Cr^{3+} standard.[2] The Fe^{3+} concentration was 2.5×10^{17} cm^{-3} while that of Cr^{2+} was 1.1×10^{16} cm^{-3}. The available signal-to-noise ratio suggests that concentrations as low as 0.5×10^{14} Fe^{3+} cm^{-3} and 1×10^{15} Cr^{2+} cm^{-3} can be determined by EPR.

X-ray-aligned single crystals were examined with a Varian E-9 X-band spectrometer. The crystals were cooled to 4.5 K by a flowing stream of He gas and could be illuminated simultaneously by monochromatic light with photon energy between 0.5 and 1.8 eV.

II. IRON-DOPED InP

A typical Fe-doped InP EPR spectrum for $\vec{H} \parallel$ [100] is shown in Fig. 1. (At high gain the weaker $|\Delta M| > 1$ transitions of Fe^{3+} also were observable at low fields.[3]) The usual five-line 8:5:9:5:8 fine structure pattern for an $S = \frac{5}{2}$ center is obscured by the overlap of the outer lines of the set, but the angular dependence unambiguously identified the spectrum as arising from Fe^{3+}($3d^5$) in cubic symmetry. The parameters determined for the usual spin Hamiltonian

$$H = g\mu_B \vec{H} \cdot \vec{S} + \frac{1}{6} a(S_x^4 + S_y^4 + S_z^4 - \frac{707}{16})$$ (1)

are given in Table I.[4]

The effect of infrared light on the intensity of the Fe^{3+} EPR spectrum in these samples is shown in Fig. 2. The ordinate represents the difference between the light-on and the light-off conditions. While these effects were purely transient (complete recovery within approximately 1 min), they are not thermal in origin as is shown by the high-energy cutoff at the band edge.

In Table I we have listed the Fe^{3+} EPR parameters and lattice constants for the III-V semiconductors GaAs,[3] GaP,[5] InAs,[6] as well as InP. This set of related compounds allows some comments to be made about the origin of the Fe^{3+} linewidths and the g values. In these compounds superhyperfine interactions with the surrounding atoms are expected to be the principal source of the Fe^{3+} EPR linewidth ΔH at low temperatures.[6] Recent electron-nuclear double-resonance results[7] allow one to conclude that this is definitely true for GaP and GaAs. Table I shows clearly that the indium hyperfine interaction makes the dominant contribution to ΔH in the indium compounds. Although no indium electron-nuclear double-resonance hyperfine data exist, the linewidth data are consistent with the rather large
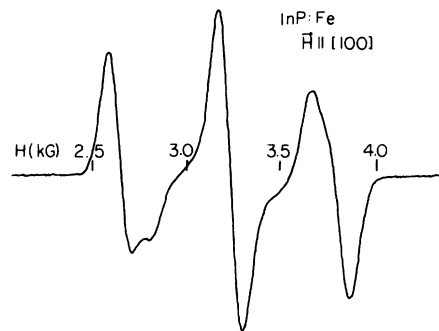

FIG. 1. X-band EPR spectrum of Fe^{3+} in InP at 4.5 K with $\vec{H} \parallel$ [100].

TABLE I.   EPR parameters of Fe^{3+} $(3d^5)$ in III-V compounds.

Compound	g	a $(10^{-4} \text{ cm}^{-1})$	ΔH (G)	a_0 (Å)	Refs.
GaAs	2.046	+340	50	5.642	3
GaP	2.025	+390	38	5.450	5,7
InAs	2.035	+421	130	6.058	6
InP	2.0235(10)	+221(2)	118(2)	5.868	This work

unpaired spin density found at gallium neighbors in the gallium compounds combined with the much larger nuclear moment of ^{115}In. From the measured linewidths, we estimate that the isotropic hyperfine constant of the nearest group-III neighbor $a(\text{In}) \simeq 20$ MHz, compared with 11.3 MHz for $a(\text{Ga})$.

The Fe^{3+} g values all show significant positive shifts from the free electron value $g_e = 2.0023$. Such shifts in covalent compounds have been attributed to electron transfer onto the central ion from the surrounding ligands.[8] We note that the significant increase in g on going from the phosphides to the arsenides is in agreement with the known decrease in the band gap and increase in the group-V ligand spin-orbit parameter.[8]

It is difficult to recognize any similar systematic trends in the value of a. The small value of a in InP is particularly difficult to understand on the presumption that iron is in the same type of site in each III-V compound. One possible solution is that a is composed of competing contributions of nearly equal magnitudes.

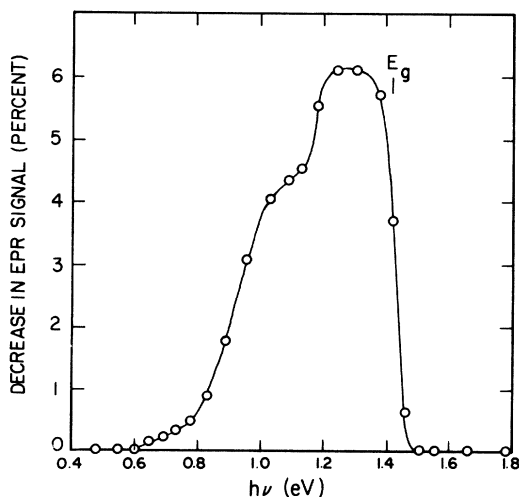The observed decrease in Fe^{3+} EPR signal with light (Fig. 2) results from transfer of electrons

FIG. 2. Change in Fe^{3+} EPR signal during application of light with photon energy $h\nu$. E_g is the band-gap energy of InP.

either on or off the Fe^{3+} ion (together with possible redistribution of population among its energy levels). Since the signal decreases with the light on, the change does not result from a photoinduced increase in relaxation rate. The principal features of the spectrum of photoinduced changes are the turn-on near 0.75 eV, the shoulder near 1.13 eV and the cutoff at the band edge E_g. This last feature illustrates that for $h\nu > E_g$ the light is stopped in a thin surface layer while EPR continues to probe the total volume of the sample, and that thermal effects are negligible. The data shown in Fig. 2 are not normalized to a constant photon flux since optical saturation effects, which would bias the normalized results, have been observed. However, the photon flux contains no anomaly near either 0.7 or 1.1 eV and there is an adequate flux below 0.7 eV; hence the features observed at these energies represent real optically induced transitions and not experimental artifacts.

The only direct optical data on Fe-doped InP is the photoluminescence work of Koschel et al.[4,9] on these same samples in which an observed luminescence at 0.35 eV is attributed to the $^5T_2 \rightarrow {}^5E$ transition of Fe^{2+} ions. This does not locate any level with respect to the band edges and hence one cannot make clear assignments of the two transitions observed here. One speculative model consistent with the luminescence results would assign the 0.75-eV transition to a direct transfer of electrons from the valence band to Fe^{3+} which converts it to Fe^{2+} in the ^5E ground state. Above about 1.1 eV, an additional transition involving electron transfer from the valence band creating Fe^{2+} in its excited $^5T_2$ state would become possible, providing an additional mode of conversion and thus decreasing the Fe^{3+} population further. It obviously would be very desirable to monitor the Fe^{2+} concentration but we were not able to detect any EPR signal due to Fe^{2+}.

III. Cr-DOPED InP

Recent work on GaAs,[10] and several II-VI compounds[11] with the zinc-blende structure, has shown that when $Cr^{2+}(3d^4)$ substitutes for Ga or a group-II atom it undergoes a static Jahn-Teller distortion
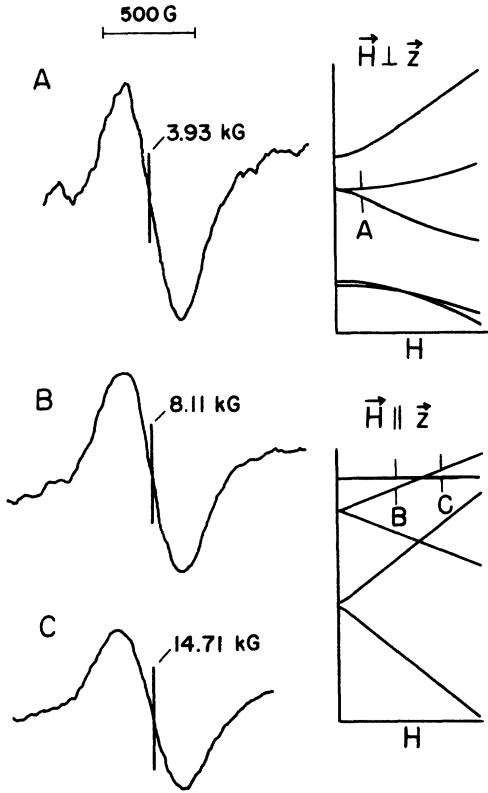
FIG. 3. X-band signals from Cr^{2+} in InP at 4.5 K, $\vec{H}$ ||[100]. The calculated energy-level diagrams indicate the origins of the resonances observed. Note that z is the local distortion axis.

at low temperatures. The local symmetry is reduced to tetragonal (actually D_{2d}) by this distortion. This leaves an orbital singlet lowest with fivefold spin degeneracy. The relevant spin Hamiltonian for such an $S=2$ system is

$$H = g_{\parallel}\mu_B H_z S_z + g_{\perp}\mu_B(H_x S_x + H_y S_y)$$
$$+ DS_z^2 + \tfrac{1}{6}a(S_x^4 + S_y^4 + S_z^4) + \tfrac{1}{180}F(35S_z^4 - 155S_z^2). \quad (2)$$

The X-band EPR spectrum of Cr^{2+} in InP at 4.5 K for $\vec{H}$|| [100] is shown in Fig. 3. Individual lines are identified in terms of the $S=2$ energy-level diagrams shown. These identifications were confirmed by other data for $\vec{H}$|| [011] and by the angular dependence of the line positions in the (01$\bar{1}$) plane. The data indicate that the low-temperature

TABLE II. Spin-Hamiltonian parameters of Cr^{2+} at 4.5 K.

Crystal	$g_{\parallel}$	$g_{\perp}$	$D - a - \tfrac{2}{3}F$ (cm^{-1})	$\lvert a \rvert$ (cm^{-1})
InP	1.981(3)	2.010(5)	−1.056(1)	0.089(7)
GaAs	1.974	1.997	−1.891	0.031

local symmetry of Cr^{2+} in InP is also D_{2d}. The spin-Hamiltonian parameters were determined by using accurately measured line positions for H along [100] and [011] and are given in Table II, where the corresponding values for Cr^{2+} in GaAs are included for comparison.

The sign of the zero-field-splitting parameter D was determined to be negative from the temperature dependence of the high-field EPR lines below 12 K. Above 12 K, all the Cr^{2+} EPR signals begin to decrease rapidly with increasing temperature and are no longer observable above 20 K. This behavior is analogous to that of Cr^{2+} in GaAs and in the II-VI compounds. We were not able to determine the sign of the cubic field parameter a from the available data although theory[11] suggests that it is positive. Also, since no transition between the low-lying pair of states and any other state could be observed, only the combination $(D - a - \tfrac{2}{3}F)$ was determined directly. During the computer fitting procedure the value of F was allowed to vary within the range $\lvert F \rvert < 0.18$ cm^{-1}; the resultant changes in the parameters shown in Table II stayed within the quoted errors. Values of $\lvert F \rvert$ substantially larger than $\lvert a \rvert$ are not expected.

We now discuss briefly the Cr^{2+} data in InP and GaAs in light of the results in II-VI compounds and the detailed analysis of Vallin and Watkins.[11] First of all, it is clear that InP is the second III-V host in which Cr^{2+} has been found to exhibit a low-temperature tetragonal Jahn-Teller distortion. This conclusion is based on the close correspondence in behavior of Cr^{2+} in InP to that in GaAs and the II-VI compounds. The only way one could produce the observed symmetry by defect association would be to have a defect complex of the form $(X - Cr^{2+} - X)$ aligned along a $\langle 100 \rangle$ direction. Besides its intrinsic unlikelihood, such a complicated defect can not explain the rapid decrease in Cr^{2+} signal above 12 K.

Second, one sees that the D and a parameters of Cr^{2+} show considerable variation with the III-V host. In the II-VI compounds a similar variation was attributed[11] to the importance of ligand wave-function admixture contributions to the spin-Hamiltonian parameters, and it is reasonable to assume that the covalent part of these admixtures will be at least as large in the III-V compounds. The order of magnitude of D and a are correctly accounted for by the theory of Ref. 11.

Third, as in the case of the II-VI compounds, the qualitative trends which relate D, $g_{\parallel}$, and $g_{\perp}$ for InP and GaAs are correctly described by theory but there are significant quantitative discrepancies. For example, following the treatment of Vallin and Watkins, the experimental D

values imply $g_\parallel(InP) = g_\parallel(GaAs) = 1.95$, $g_\perp(InP)$
$= 2.04$ and $g_\perp(GaAs) = 2.03$. Thus, the theory over-estimates the g tensor deviations from the free-electron value. It is of interest, however, that InP represents the first host in which the experimental $g_\perp$ for Cr^{2+} is greater than g_e as the theory predicts.

Finally, we call attention to the large super-hyperfine-broadened EPR linewidths for Cr^{2+} in InP (Fig. 3). Typical linewidths for Cr^{2+} in InP are in the range 300–350 G for H along high-symmetry directions. Comparing linewidths for equivalent EPR transitions, one finds that $\Delta H(InP)$ $\simeq 3.4\Delta H(GaAs)$. This result implies that there is a substantial superhyperfine interaction between Cr^{2+} and the group-III neighbors (Ga, In). In this respect Cr^{2+} resembles Fe^{3+} although the Cr^{2+} center wave functions must be significantly more de-localized.

In InP, we have looked for EPR signals arising from Cr^{3+} similar to those in GaAs,[12] but none have been found. Furthermore, unlike the situation for Cr^{2+} in GaAs,[10] we have not been able to induce changes in the Cr^{2+} EPR signal for InP by optical illumination. Changes as small as 10% should have been detected easily. Thus, for the samples examined, it appears that Cr behaves rather differently in InP than in GaAs.

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Reference 11 below cites arguments for transition metals being substitutional. We consider the question unresolved; either undistorted site has tetrahedral symmetry and we assume throughout that both Fe and Cr are substitutional in group III sites.

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