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SPIN DEPENDENT CARRIER CAPTURE PROCESSES OBSERVED BY ODMR ON THE 0.84 eV LUMINESCENCE IN SI-GaAs:Cr

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Optically detected magnetic resonance (ODMR) observed on the 0.84eV Cr-related emission in semi-insulating GaAs:Cr implies that the excited state associated with this internal transition of the axial $[\mathrm{Cr}^{2+}\text{-X}]$ centre is formed by the spin dependent free carrier capture process: $[\mathrm{Cr}^{3+}\text{-X}] + e_{CB} \rightarrow [\mathrm{Cr}^{2+}\text{-X}]^*$
The results imply that the luminescence is not due to the presence of $[\mathrm{Cr}^{2+}\text{-X}]$ ground state centres in the material as previously assumed. A competing charge transfer process, possibly involving $[\mathrm{Cr}^{4+}]_{Ga}$, is observed as a quenching ODMR signal on the 0.84eV luminescence.

Introduction

The observation of ODMR in semiconductors has established many spin dependent radiative and non-radiative processes which have recently been reviewed (1). Bound triplet exciton and donor-acceptor pair recombination has been characterized in considerable detail but recombination at deep traps such as those associated with transition metal ions is less well understood. Recently, studies of Cu in ZnSe (2)(3) and ZnS (4) have made some progress in this field. This communication presents results which are interpreted in terms of a free carrier capture process in GaAs:Cr where above band gap excitation creates spin polarized free carriers. Subsequent electron capture at axial $[\mathrm{Cr}^{3+}\text{-X}]$ centres produces the excited state involved in the 0.84eV radiative transition, which is due to an internal transition of trigonal $[\mathrm{Cr}^{2+}\text{-X}]$ centres (5)(6). Evidence is also presented for a charge transfer process involving $[\mathrm{Cr}^{4+}]_{Ga}$ which competes with the radiative process. Previously it has been assumed that the luminescence is due to a direct excitation of $[\mathrm{Cr}^{2+}\text{-X}]$ centres present in the material. Our results suggest that this is not the case and that the ground state of the process is the trigonal defect $[\mathrm{Cr}^{3+}\text{-X}]$.

Experimental

The principles and techniques of ODMR have been reviewed by Cavenett (1). The ODMR measurements reported here were carried out using a split-coil superconducting magnet in the Faraday configuration, at 9.0GHz, with the samples at 2K. Excitation of the sample, mounted in the microwave cavity, was accomplished using circularly polarized 752nm or 799nm radiation (above band gap excitation) from a Coherent Radiation CR3000K krypton ion laser. Luminescence was detected by a North Coast Ge detector, via a Si filter and neutral density filters (to avoid saturation of the detector) or a Hilger and Watts 0.3m spectrometer. The samples for which ODMR signals were observed were Sumitomo SI-GaAs, which in fact were double doped with Cr and O.

Experimental Results

Figure (1) (lower curve) shows the luminescence excited with 799nm radiation. The no-phonon line (NPL) is at 0.838eV and a weak underlying band with NPL at an estimated energy of ∿ 0.9eV can also be observed. This latter band is particularly strong with 1.06µ Nd:YAG excitation (see figure (1) upper curve). The ODMR spectra for B// <100> are shown in figure (2) where the upper curve (a) was recorded using linearly polarized excitation, the central curve (b) was recorded with $\sigma+$ excitation and the curve (c) was recorded with $\sigma-$ excitation. Three lines labelled A, B and C are observed for $\sigma+$ polarization though the variation of shape of the central line at $g = 1.93 \pm 0.06$ under different experimental conditions indicates that there are two signals in this region, one with positive ΔI and the other, the stronger resonance (B), with ΔI negative (and the smaller g-value). The spectral dependences were measured using the monochromator and are shown in figure (3). This measurement confirms that the signals are related to the 0.84eV emission. Note that for the underlying band with NPL at ∿ 0.9eV a signal with a g-value similar to that of resonance B is observed as an increase in light suggesting that this emission is a competing process to the 0.84eV emission.

Detailed angular dependence studies are shown in figure(4). The splitting of resonance A, which corresponds to a positive ΔI, implies that all centres associated with this signal are equivalent for B//<100> suggesting a <111> oriented defect. Lines B and C are isotopic within the experimental errors.

Discussion

The 0.84eV Cr-related luminescence in SI-GaAs:Cr has been variously attributed to FB or DAP recombination (7)(8), conduction band → $[\mathrm{Cr}^{2+}]_{Ga}$ $^5T_2$ ground state transition (9)

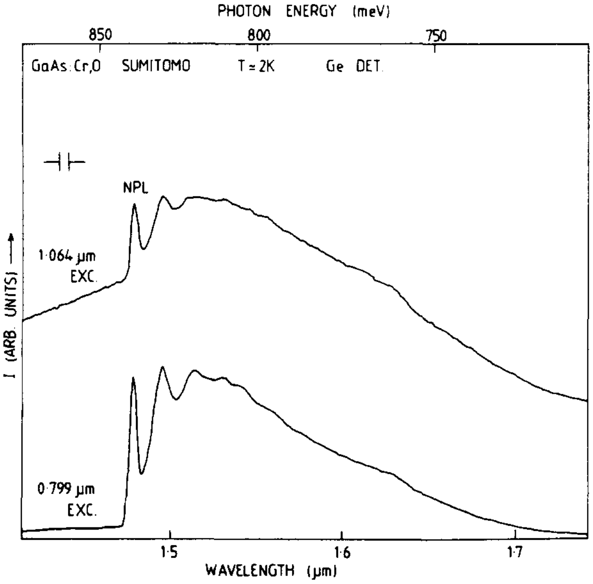

Fig. 1. Photoluminescence obtained from the Sumitomo material using above (0.799µm) and below (1.064µm) band gap excitation showing the 0.84eV band, together with the broad underlying band.

and the internal transition $^5E \rightarrow {}^5T_2$ of $[Cr^{2+}]_{Ga}$ (10)(11). However, high resolution cathodoluminescence and absorption measurements performed on the 0.838eV no-phonon line system, by Lightolwers, Henry and Penchina (12)(13), established the existence of considerable fine structure in the 0.838eV spectrum. An empirical level scheme was proposed from the temperature dependence of this data, which was clearly incompatible with the level scheme for $[Cr^{2+}]_{Ga}$ deduced from EPR (14) and from far infra-red absorption measurements (15). Subsequent Zeeman measurements on the 0.838eV no-phonon line system, reported by Killoran et al (5)(6) and Eaves et al (16)(17), implied that the Cr-associated impurity centre responsible for the 0.84eV emission has C_{3v} axial symmetry and therefore is not the $[Cr^{2+}]_{Ga}$ centre which exhibits a tetragonal static Jahn Teller distortion (14).

Although White (18) proposed that the 0.84eV emission can be attributed to excitonic recombination at isoelectronic sites involving Cr, by analogy with the Zn-O associate in GaP (19), it would appear more reasonable to assume that this luminescence is due to a Cr^{2+} ion $^5E \rightarrow {}^5T_2$ transition perturbed by a C_{3v} crystal field, particularly in view of the fact that the $[Cr^{2+}]_{Ga}$ $^5T_2 \rightarrow {}^5E$ internal transition has recently been detected in absorption (20) and photoconductivity (21) at 0.825eV. Models for the 0.84eV centre based upon this assumption, with the C_{3v} crystal field arising due to an additional nearest neighbour impurity, have been presented by Picoli et al (22)(23) and Voillot et al (24)(25). The lowering of symmetry results in a splitting of the $^5T_2$ (T_d) orbital state into a $^5A_1$ and a lower lying ^5E (C_{3v}) state (the ^5E (T_d) excited state becomes $^5E^*$ (C_{3v})) in the absence of Jahn-Teller effects. Both these models include dynamic Jahn-Teller effects in the description of the impurity states.

The model of Voillot et al (24)(25), which involves an almost total quenching of the trigonal crystal field in the ground state of the $[Cr^{2+}\text{-}X]$ centre by a dynamic Jahn-Teller interaction, was initially proposed to fit their high resolution luminescence spectroscopy and thermal activation measurements (24). This data resulted in a reinterpretation of the zero magnetic field excited and ground state level scheme of Lightowlers et al (12)(13) for the 0.84eV system. Voillot et al (25) subsequently obtained a fit to the Zeeman data of Killoran et al (5)(6) using this model and have since applied this description to the analysis of uniaxial stress measurements on the 0.838eV no-phonon line system (26) and phonon scattering data obtained from GaAs:Cr (27).

The compatibility between the symmetry properties of the ODMR signal A and the Zeeman splittings of the 0.838eV no-phonon line system led to our initial proposal (6) that signal A was the result of resonant microwave modulation of the $^5E^*$ excited state of the $[Cr^{2+}\text{-}X]$ centre. However, attempts by us and Voillot et al (28) to reconcile this proposal with the spin-orbit and magnetic splittings determined for the $^5E^*$ state were not successful and we therefore have had to reconsider the interpretation of the ODMR data. In fact, a comparison of our results, for signal A, with the EPR data of Whitehouse et al (29) for Cr associated trigonal centres in electron irradiated p-type GaAs:Cr,Zn suggests that we are observing a similar type of centre in ODMR. These authors observed the resonance occurring in the $|\pm\frac{1}{2}\rangle$ ground state doublet of

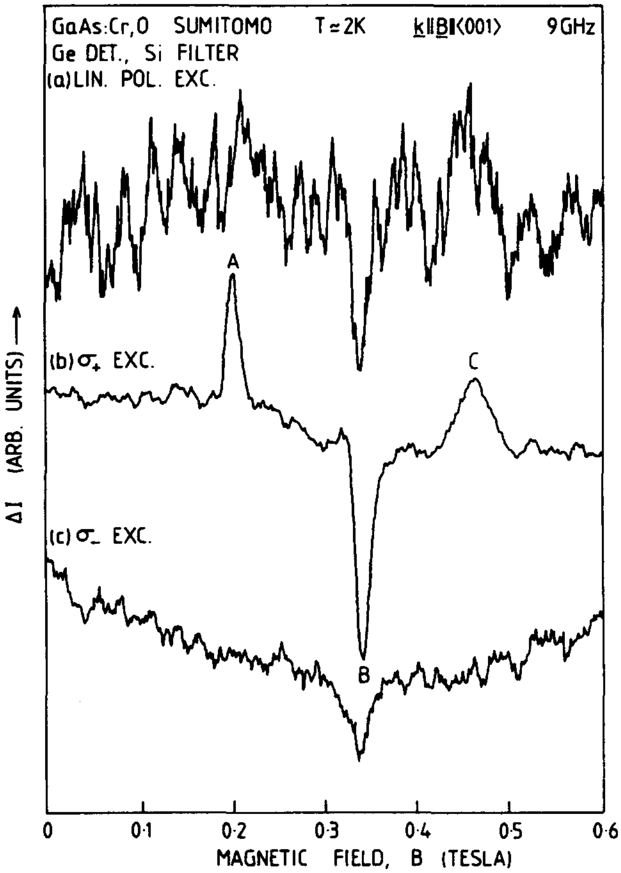

Fig. 2. ODMR signals at 9 GHz obtained by monitoring the 0.84eV photoluminescence from the Sumitomo material with (a) linearly polarized excitation; (b) and (c) optical pumping with circularly polarized exciting light σ+ and σ− respectively.

trigonally distorted Cr^{3+} ions, i.e. $[Cr^{3+}-X]$ where X in this case is thought to be an intrinsic irradiation induced defect, e.g. $[Ga]_I$, and the Cr ion is substitutional on a Ga site. The ^4F ground term of the $3d^3$ ion is split to give a $^4A_2$ orbital singlet ground state in C_{3v} symmetry and the inclusion of a first order spin-orbit interaction results in the S = 3/2 ground state being split into two doublets, $|\pm 3/2\rangle$ and $|\pm\frac{1}{2}\rangle$, separated by 2D if the following spin Hamiltonian is used:

$$\mathcal{H} = D\left[S_z^2 - \frac{1}{3}S(S+1)\right] + \mu_B\left[g_\parallel B_z S_z + g_\perp (B_x S_x + B_y S_y)\right].$$

In the weak-field approximation it can be shown that the lower lying $|\pm\frac{1}{2}\rangle$ doublet can be treated as an effective spin $S = \frac{1}{2}$ system, the corresponding effective g-values being given by:

$$g'_\parallel = g_\parallel$$
$$g'_\perp = g_\perp\,(S + \tfrac{1}{2})$$

where $g_\parallel \approx 2.0023$

$g_\perp < 2.0023$

Whitehouse et al (29) obtained the following parameters on the basis of this model:

$$g_\parallel = 2.0098$$
$$g_\perp = 1.977$$
$$2D = \lambda\,(2.0023-g_\perp) = 2.3\ \text{cm}^{-1}$$

where a value of 90 cm^{-1} was used for the free-ion spin-orbit coupling coefficient λ. Using the same analysis we obtain for line A of our ODMR data:

$$g_\parallel = 2.13 \pm 0.05$$
$$g_\perp = 1.89 \pm 0.03$$
$$2D \approx 10.1\ \text{cm}^{-1}$$

This model is successful in describing both sets of data, although Whitehouse et al (29) note that a higher value of effective spin, S (e.g. S = 5/2) could lead to the observed g-values but in that case a theoretical fit would require a fortuitous (and therefore unlikely) ratio of crystal field parameters.

The materials studied by the two techniques are very different since in the ODMR experiment device grade substrate material was examined whilst highly irradiated bulk material was studied by EPR (29). However, it is clear from a comparison of the results that, although the observed centres are not precisely the same in the two materials, the ODMR signal A and the EPR (29) are both associated with the ground states

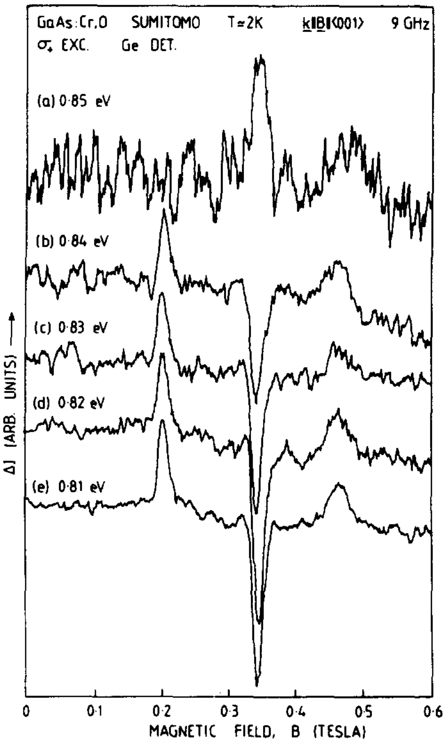

Fig. 3. ODMR signals obtained at different emission energies, illustrating the spectral dependence of the signals with respect to the 0.84eV and 0.9eV bands.

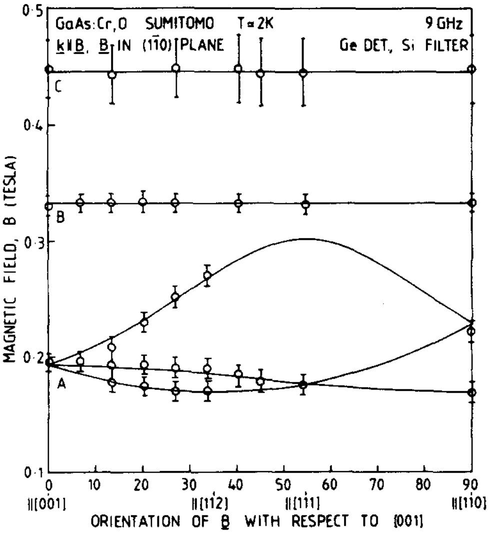

Fig. 4. The angular dependence of the ODMR signals, A, B and C for rotation of the magnetic field in the $(1\bar{1}0)$ plane. The open circles correspond to data points, with the half widths of the signals indicated by the bars. A theoretical fit (solid lines) is also shown and is discussed in the text.

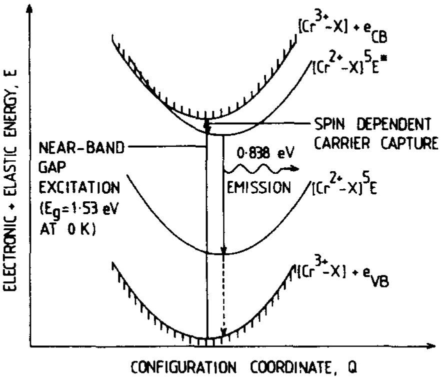

Fig. 5. Configurational coordinate diagram showing excitation and emission processes involving [Cr-X] centres in SI-GaAs:Cr.

of [Cr^{3+}-X] centres. This assignment and the optical pumping results imply that the formation of the [Cr^{2+}-X] ^{5}E* excited state occurs via a spin-dependent free carrier capture process involving the [Cr^{3+}-X] ^{4}A$_2$ ground state of the same impurity complex. Emission of the 0.84eV band de-excites the centre to the [Cr^{2+}-X] ^{5}E state and hole capture returns the centre to the ground state. These processes are summarized as follows:

$$h\nu_{\text{excitation}} \rightarrow e_{CB} + h_{VB}$$
$$e_{CB} + [Cr^{3+}\text{-}X]\ {}^4A_2 \rightarrow [Cr^{2+}\text{-}X]\ {}^5E^*$$
$$[Cr^{2+}\text{-}X]\ {}^5E^* \rightarrow [Cr^{2+}\text{-}X]\,{}^5E + h\nu_{0.84eV}$$
$$[Cr^{2+}\text{-}X]\ {}^5E + h_{VB} \rightarrow [Cr^{3+}\text{-}X]\ {}^4A_2$$

A configurational coordinate diagram illustrating the excitation and recombination paths is shown in figure (5). We have considered the alternative possibility that [Cr^{2+}-X] ^{5}E is the ground state for this system and that [Cr^{3+}-X] ^{4}A$_2$ is formed by hole capture prior to the formation of [Cr^{2+}-X] ^{5}E*. This model would require that [Cr^{3+}-X] ^{4}A$_2$ is an excited state with a lifetime sufficiently long for thermalization to occur. Also, **trigonal Cr**$^{2+}$ centres in GaAs:Cr have not been observed so far by ground state EPR. At this stage of the investigation therefore we believe that this alternative model is less likely.

So far we have only considered the anisotropic signal A in figure (2). The isotropic line B with g = 1.93 ± 0.06 is a decrease in the 0.84eV emission intensity and can be attributed to [Cr^{4+}]$_{Ga}$ centres formed on laser excitation which take part in a charge transfer process that competes with the 0.84eV emission. For example, after bandgap excitation hole capture converts [Cr^{3+}]$_{Ga}$ to [Cr^{4+}]$_{Ga}$. Then the excited [Cr^{2+}-X] ^{5}E* state can de-excite by a spin dependent electron-hole transfer with the [Cr^{4+}]centre in a similar manner to that suggested by Stauss et al (30). These processes can be summarized as follows:

$$[Cr^{3+}]_{Ga} + h_{VB} \rightarrow [Cr^{4+}]_{Ga}$$
$$[Cr^{2+}\text{-}X]\ {}^5E^* + [Cr^{4+}]_{Ga} \rightarrow [Cr^{3+}\text{-}X]^4A_2 + [Cr^{3+}]_{Ga}$$

The curve (a) in figure (3) shows that a g = 2 resonance with positive ΔI occurs on the broad underlying 0.9eV band suggesting that this band may be the radiative energy dissipated in the above de-excitation process. Note that the resonance C also occurs on the 0.9eV band but so far we have no explanation for the origin of this signal.

The optical pumping dependence of the ODMR signals provides the key to the understanding of these results since it is well established that near bandgap excitation in a material such as GaAs with E$_g$ ≈ Δ, the spin orbit splitting of the valence band, results in spin polarization of the conduction electrons of up to 25% (31). These polarized electrons combine with [Cr^{3+}-X] centres by a spin dependent carrier capture process. In a magnetic field the lowest state of the [Cr^{3+}-X] centre can be considered as a spin $S = \frac{1}{2}$ doublet and the ODMR monitors the change of conduction band electron capture rate as the spin of the thermalized [Cr^{3+}-X] doublet is changed at resonance. The process is somewhat analogous to a DAP recombination, though in the present case the final state is one of the [Cr^{2+} -X] ^{5}E* manifold. Details will be published elsewhere (32).

We can conclude that the ODMR allows the observation of the ground state of the defect which gives rise to the 0.84eV emission. A comparison of our data for the resonance A with the EPR results for electron irradiated GaAs:Cr,Zn (29) implies that this ground state is that of trigonally distorted Cr^{3+}, where the C$_{3v}$ symmetry of the system is most probably due to a neighbouring impurity. Excitation with near-bandgap radiation results in free electron capture at the [Cr^{3+}-X] centres to form [Cr^{2+}-X] centres in the ^{5}E* excited state which decay to the [Cr^{2+}-X] ^{5}E ground state giving the 0.84eV emission. Thus, the 0.84eV luminescence in SI-GaAs:Cr originates from an excitation of Cr^{3+} centres, with <111> symmetry, present in the as grown material in concentrations smaller than can be observed by conventional EPR (∿ 10^{14}-10^{15} cm^{-3}). Electron irradiation of GaAs:Cr,Zn creates similar <111> axial Cr^{3+} centres in much larger concentrations.

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