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THE MAGNETIC FIELD AND UNIAXIAL STRESS DEPENDENCE OF THE Cr-RELATED PHOTOLUMINESCENCE OF GaP(Cr)

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The intense 1.03 eV photoluminescence line in Cr-doped GaP is studied using Zeeman and piezo-spectroscopy and is shown to arise from a Cr-related (100) axial defect.

The deep level photoluminescence (PL) associated with the presence of Cr in III-V compounds has been the subject of great interest recently. The famous 0.84 eV PL in GaAs(Cr) is now known to arise from recombination at (111) axial defects involving Cr *[1-4]*. The Cr-related PL spectrum of GaP is superficially rather similar to that of GaAs. A sharp zero phonon structure is observed at 1.03 eV with broader phonon sidebands at lower energy. This structure was first related to the presence of Cr by Kaufmann and Koschel *[5]* although it had previously been observed by Dean *[6]* in nominally pure material.

In this paper we report Zeeman and piezo-spectroscopy on the 1.03 eV line and show that it arises from recombination at Cr-related defects with (100) axial symmetry. The difference in symmetry of these defects in GaP and GaAs is strikingly revealed by the anisotropy of the Zeeman spectra.

The GaP crystals used were grown by MCP Ltd. using the LEC method and were analyzed by mass spectroscopy at Plessey Research (Caswell). Table 1 lists the principal impurities. The high concentration of Cr makes the material semi-insulating.

Table 1 Principal impurities from mass spectrography (all others < 4×10^{15} cm^{-3})

Element	B	C	N	O	Na	Si	S	Cl	Ca	Cr	As
Conc. (10^{17} cm^{-3})	0.3	$\leq$ 4.0	$\leq$ 1.5	$\leq$ 30	0.05	0.05	0.5	0.05	0.05	4.0	0.2

The PL spectra were obtained using a 0.75 m or 1 m grating monochromator and a cooled intrinsic Ge detector. The samples were immersed directly in superfluid helium at 2 K and illuminated with 40 to 80 mW of the 488 nm or 514.5 nm lines from an Ar ion laser. Figure (1) shows the zero phonon PL structure, consisting of a strong central triplet with two weaker triplets symmetrically placed on either side.

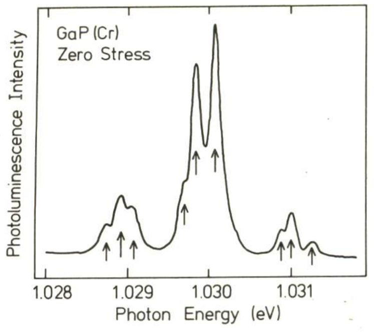

FIGURE 1 the zero phonon fine structure in the PL spectrum of GaP(Cr) at 2 K (zero magnetic field and zero uniaxial stress)

As the magnetic field B is increased the lines split in a slightly non-linear fashion and the intensities of some components change rapidly, presumably due to thermalization effects. Figure (2) shows typical spectra at 10 T for B parallel to the three principal symmetry axes. The magnetic field was generated by the 10 T split coil superconductor at MPI, Grenoble.

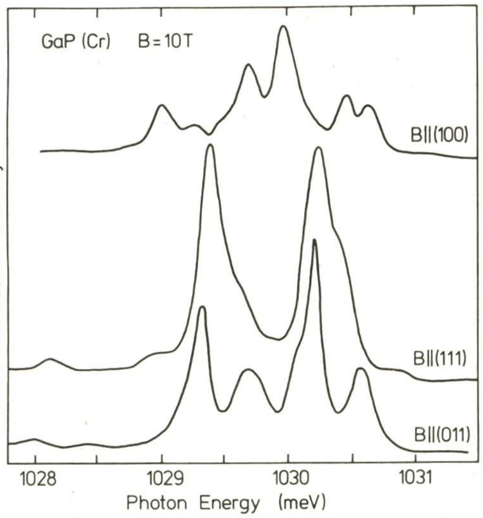

FIGURE 2 the Zeeman-split zero phonon system at 10 T with B parallel to the three principal axes

That the PL arises from recombination at axial defects is shown most graphically by plotting the anisotropy of the Zeeman spectrum as the magnetic field is swept through one of the principal crystalline planes. The data points in Figures (3) and (4) show the results when B = 10 T is swept through the ($0\bar{1}1$) and (001) crystal planes. The plot for the ($0\bar{1}1$) plane shows crossing points and a simplification of the spectrum when B is parallel to a (111) direction. This, and the overall form of the anisotropy, points to recombination at defects with principal symmetry axes along the three equivalent (100) axes. The following procedure has been used to verify that simple (100) axial defects will yield the observed anisotropy. The sections of Figure (3) corresponding to recombination at the defects with their principal axes in the ($0\bar{1}1$) plane have been used to generate Figure (5) which plots the recombination energy for a given defect orientation as a function of the angle ϕ between B and the principal axis of the defect. From this figure the energy of recombination for the remaining defect orientations can be deduced by calculating the angle between the defect axis and B.

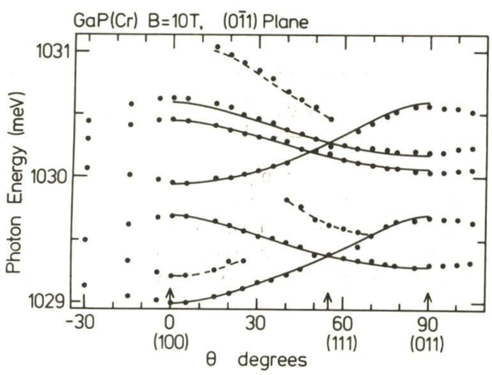

FIGURE 3 the Zeeman anisotropy at 10 T with B rotated in the ($0\bar{1}1$) plane: The data points agree well with the predictions of a simple (100) axial defect model (solid lines). See also Figure (4)

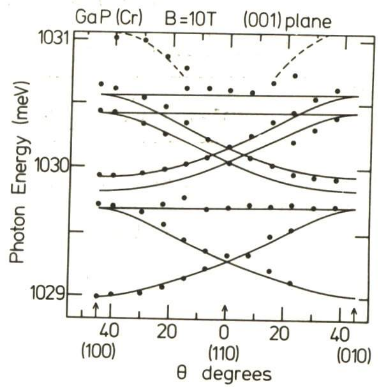

FIGURE 4 the Zeeman anisotropy at 10 T with B rotated in the (001) plane

The solid lines in Figures (3) and (4) are the results of such a procedure and are in excellent agreement with the data points. The dotted lines shown in the figures correspond to transitions which become too weak to follow over the whole angular range.

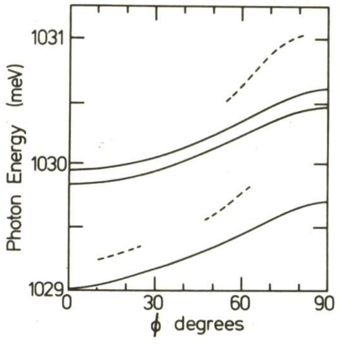

FIGURE 5 variation of the recombination energy as a function of ϕ, the angle between B and the principal axis of the defect: The curves are deduced from the data points in Figure (3)

Our results show that the Cr-related defect in GaP which gives rise to the prominent deep level PL has a quite different axial symmetry from that found in GaAs. The (111) axial symmetry for GaAs(Cr) is consistent with a simple model involving Cr substitutional on a Ga-site (Cr_{Ga}) and a second impurity on the nearest-neighbour As site. This is closely analogous to the Cd-O complex found in GaP [7]. Let us now consider the ways in which a (100) axial defect might arise. Stauss et al. [8] have pointed out that (100) axial defects can only be produced by an aligned three-defect complex of the form (X-Cr-X). Such a complex seems extremely implausible. An interstitial defect would give rise to C2v rather than the D2d symmetry suggested by the Zeeman anisotropy data. It is known from EPR measurements that the ground state of substitutional Cr^{2+} in InP [8] and GaAs [9] exhibits a tetragonal Jahn-Teller (J-T) distortion and hence has the required axial symmetry to explain our Zeeman PL data. However, care is needed in comparing these types of experiment as they are performed in quite different magnetic field regimes. If a small orthorhombic component existed it could become suppressed in the high magnetic field regime used in the Zeeman measurements. Hence even a (111) nearest-neighbour axial complex undergoing a strong tetragonal J-T distortion cannot be ruled out as a possible explanation of the Zeeman PL results. It is worth mentioning that our Zeeman data in GaAs(Cr) indicate the presence of an additional dynamic J-T distortion of the (111) axial complex.

In order to test whether a tetragonally distorted state of Cr in GaP is involved in the recombination process giving rise to the 1.03 eV PL, we have investigated the effect of uniaxial stress on the spectra. Figure 6 shows the results for compressive stress T // (100). The energies of two groups of lines shift at equal, but opposite, rates with increasing stress. The intensity of the group moving to higher energy decreases rapidly due to a thermalization effect. Unless the hydrostatic component produces a fortuitous compensation, one would expect rigid (100) axial defect complexes to split at rates in the ratio 2:1. In addition, it is hard to envisage how such a model could explain the thermalization effect. The

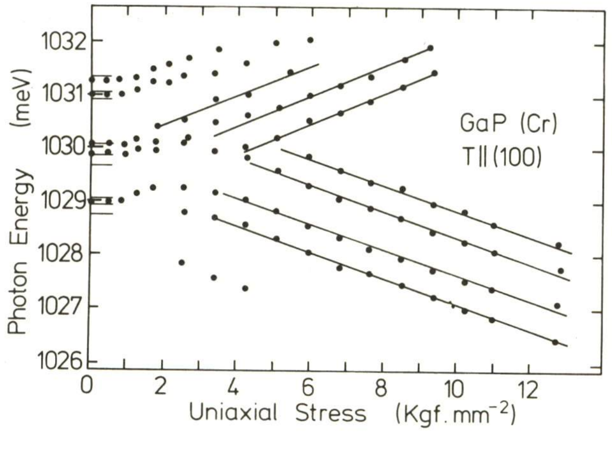

FIGURE 6 the uniaxial stress dependence for compressive stress T // (100): The lines moving to higher energies disappear due to thermalization stress results therefore seem to favour a model involving a tetragonally distorted J-T system. Although the simplest model for such a system is therefore a simple substitutional Cr ion on a Ga-site, the possibility of a complex involving Cr and another impurity must be considered (10).

Finally, it is worth noting that the possibility of a Cr,O complex has been investigated by studying the PL of material containing Cr and ^{18}O enriched oxygen (M. S. Skolnick and P. J. Dean, private communication). No changes that might have arisen from an isotopic shift of the zero phonon 1.03 eV PL fine structure could be observed.

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