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PHOTOLUMINESCENCE FROM DEEP CENTERS IN GaAs†

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Sharp line structure attributable to phonon assisted radiative emission has been observed in the 6 K photoluminescence spectra from deep centers in bulk samples of chromium doped GaAs. Two luminescence bands at 0.56 and 0.8 eV have been observed and both bands exhibit evidence of phonon assisted radiative recombination. An explanation of these luminescence bands in terms of excited state to ground state transitions of Cr^{3+} and Cr^{2+} ions is proposed.

SEMI-INSULATING bulk GaAs is of current technological importance since this material is often used as base material for ion implanted devices or as substrates for epitaxial films. Semi-insulating GaAs is usually produced by Cr doping to compensate shallow donor impurities. However, little is known at present about the way that Cr is incorporated into the GaAs lattice and the energy states formed by this transition metal impurity. Energy levels deep in the forbidden gap of GaAs:Cr have been studied by various techniques, e.g. i.r. absorption,[1,2] photoconductivity,[3] capacitance spectroscopy,[4] and temperature dependence of the dark conductivity.[5] These studies suggest that chromium forms an impurity state near the center of the forbidden gap and that this state acts as an acceptor.

Near band edge photoluminescence has been studied extensively in GaAs, and observed luminescence bands have been correlated in some detail with various impurities.[6,7] In contrast, very limited information concerning deep impurity levels in GaAs:Cr has been obtained thus far from photoluminescence experiments. Allen[8] and others have reported a broad luminescence band at 0.8 eV at 80 K which has been attributed to recombination involving Cr impurities; additional bands centered at 0.56 and 0.63 eV have been observed at 80 K by Peka and Karkhanin[9] in GaAs:Cr. A broad band at approximately 0.6 eV has been observed by Turner *et al.*[10] in GaAs:O.

We have studied the low temperature (6 K and 80 K) "deep" photoluminescence spectra of several GaAs:Cr samples and of one undoped GaAs sample. In all of the bulk chromium-doped samples bands centered at about 0.8 and 0.56 eV were observed. At the lowest temperatures (6 K) in most cases sharp structure appears on both bands which we attribute to multiple phonon emission. To our knowledge this is the first observation of such structure for near mid-gap luminescence centers. In addtion, the simultaneous observation of both bands in all GaAs:Cr samples when combined with additional information is suggestive that both bands (0.56 and 0.8 eV) are, in some way, due to chromium centers.

The luminescence measurements were carried out in the spectral range from 0.4 to 1.5 eV with the 6471 Å line of a krypton laser for excitation. The luminescence was analyzed by a Spex 3/4 m grating monochromator and detected by a cooled PbS photoconductor. Chromium-doped bulk GaAs samples were obtained from Monsanto, Laser Diodes, Inc., and Siemens A.G., and were compared with samples grown at NRL. The samples had resistivities in the range 10^6–10^8 Ω cm at 300 K. For the sake of comparison, a non-intentionally doped low resistivity sample of GaAs obtained from Laser Diodes, Inc., and a Cr-doped liquid epitaxial layer[11] were also investigated. Most of the samples were analyzed by ion beam mass spectroscopy and were found to contain Cr and Si in varying amounts. The Monsanto sample contained the most Cr and Si.

Figure 1 shows the observed luminescence spectra for the Monsanto sample at 6 and 80 K. All of the bulk chromium-doped samples exhibited spectra similar to those of Fig. 1; in all cases the previously reported 0.8 and 0.56 eV bands were observed. These two bands are always observed together in the bulk material, that is, one does not observe the one band without the other. Their relative intensities do vary from sample to sample and they do change with temperature as seen in Fig. 1. In addition, structure was observed for the first time in both bands at low temperature (6 K). A sharp line at 0.837 eV is clearly evident in the 6 K spectrum of Fig. 1 and it is identified as the zero phonon line for the

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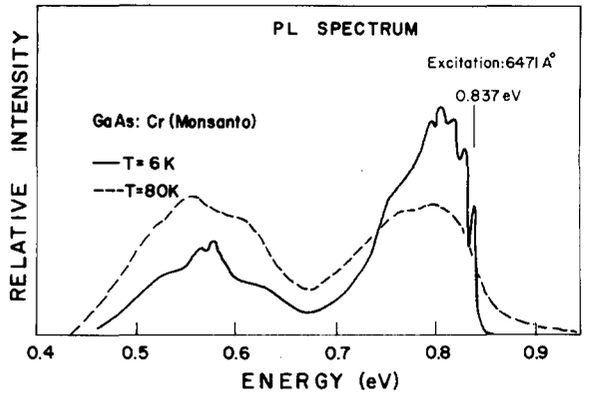

Fig. 1. Photoluminescence spectra of GaAs:Cr at 6 K and 80 K with 6471 Å krypton laser excitation.

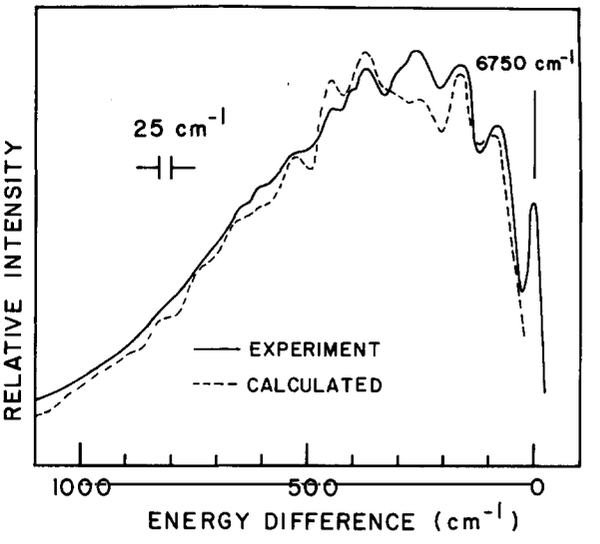

Fig. 2. Experimental and calculated luminescence intensity distribution for the 0.8 eV band. The sharp zero phonon line is located at 6750 cm^{-1} (0.837 eV). The resolution for the experimental spectrum was ~ 25 cm^{-1}.

0.8 eV band. No sharp zero phonon line was observed for the 0.56 eV band. It is possible that this line is obscured by the presence of an oxygen-related luminescence band in the vicinity of 0.6 eV which could be responsible for the boradened high energy portion of the 0.56 eV band. The zero phonon line at 0.837 eV is attributed to a localized transition at the chromium ions and will be discussed in a later section. The additional lines or side bands in the 0.8 eV band occur at energy separations from the zero phonon line which correspond to zone boundary and zone center phonon modes of GaAs. An energy difference scale is shown in Fig. 2. The first side band at an energy separation of 78 cm^{-1} corresponds closely to the 79 cm^{-1} energy of the TA(X) phonon measured by inelastic neutron scattering.[12] A peak in the one phonon density of states in GaAs may be expected at this energy, since the second order Raman cross-section shows a peak[13] at roughly 160 cm^{-1}. The next luminescence side band was observed at 160 cm^{-1} and corresponds to two zone boundary TA phonons. In addition, the coupling of the LO(Γ) phonon (with energy 296 cm^{-1} at low temperature)[14] has to be considered.

Similar phonon related structure has been observed in the luminescence spectra arising from certain shallower impurities in GaAs such as Sn[15] and Ag.[16] In conjunction with these observations it was pointed out[17] that the phonon coupling becomes stronger with increasing depth of the impurity level, since the sharply varying potential associated with a deep impurity has large wave vector Fourier components which couple well with zone boundary phonons. On this basis, a strong phonon coupling for the 0.8 eV band in GaAs:Cr is a reasonable expectation.

It is possible to obtain a qualitative or approximate representation of the phonon coupled emission lineshape of the 0.8 eV band through the use of the theory of Hopfield.[18] If only lowest or first order terms in the electron–phonon interaction are considered, a Poisson distribution is obtained for the probability of emission of n phonons with the simultaneous emission of a photon[19]

$$W_n = \exp(-\bar{N}^n)\cdot\frac{\bar{N}}{n!}, \tag{1}$$

Where $\bar{N}$ represents the average phonon coupling parameters, $\bar{N}_{TA}$ for the acoustical phonons and $\bar{N}_{LO}$ for the LO phonons. If it is assumed, as suggested above, that the general features of the 0.8 eV band can be described in terms of the contributions of the LO(Γ) and TA(X) phonon modes for GaAs, then the relative intensities contributed by different phonon combinations are given by

$$I(E) = \sum_{n_1 n_2} \frac{\bar{N}_{TA}^{n_1}}{n_1!}\frac{\bar{N}_{LO}^{n_2}}{n_2!}\frac{1}{1+(E-E_0-E_{n_1+n_2})^2/\gamma^2}, \tag{2}$$

where E_0 is the energy of the zero phonon emission and

$$E_{n_1+n_2} = n_1 E_{TA} + n_2 E_{LO} \tag{3}$$

is the energy of the multiphonon emission. The phenomenological broadening parameter γ is introduced to account for phonon lifetime broadening as well as broadening due to contributions from the phonon density of states.

A comparison of the experimental lineshape of the 0.8 eV luminescence band with the best fit generated by the theoretical intensity distribution of equation (2) is shown in Fig. 2. The parameters used to calculate this intensity distribution are $\bar{N}_{TA} = 2.1$, $\bar{N}_{LO} = 0.9$,

and $\gamma = 44\ \text{cm}^{-1}$. The close correspondence between the prominent features and overall lineshape of the experimental and theoretical spectra in Fig. 2 appears to justify the conclusion that electron–phonon interactions give rise to the structure of the 0.8 eV luminescence band. The general features of the 0.56 eV band are also consistent with phonon coupling. However, a detailed interpretation of this band is precluded by the absence of a distinct zero phonon line.

As pointed out previously, the 0.8 eV band has been attributed[8,9] to the presence of chromium in the GaAs. It is likely that the chromium atoms occupy gallium sites in the GaAs crystal lattice. In this case the charge of the uncompensated chromium atoms would be Cr^{3+}, while the compensated chromium's would be in the Cr^{2+} state. Thus it may be expected that when high purity GaAs containing few donors is chromium doped, most of the chromium will be in the Cr^{3+} state. Conversely, chromium doping of GaAs which contains a large concentration of donors to be compensated, results in many chromium atoms in the Cr^{2+} state. The 0.8 eV luminescence observed in chromium doped GaAs might well be attributed to transitions between the ^5E and $^5T_2$ crystal field levels of Cr^{2+} in tetrahedral coordination. Furthermore, the 0.9 eV peak in optical absorption observed in GaAs:Cr[1] could be assigned to the same transition at Cr^{2+} sites. The difference between the 0.8 eV luminescence band and the 0.9 eV absorption band is attributed to the strong lattice coupling; this causes the peak of the emission band to occur at an energy *below* the zero phonon line, and the peak in the absorption band to occur at an energy *above* the zero phonon line. Perhaps, the strongest evidence for this assignment is provided by the optical absorption data of Ippolitova *et al.*[2] These workers observed that when tin dopants (donors) were added to chromium doped GaAs, thereby producing Cr^{2+} by compensation, a strong absorption line at 0.9 eV was observed. Conversely, they observed no 0.9 eV peak in the optical absorption in high purity chromium doped GaAs which would be expected to contain primarily Cr^{3+}. A peak in *n*-type photoconductivity at 0.9 eV[8] is also reported in GaAs:Cr. From this it can be concluded that the excited state of Cr^{2+} must be close to the bottom of the conduction band. The ground state energy is then about 0.67 eV above the valence band. From a careful evaluation of the temperature dependence of the dark conductivity, a value of 0.69 eV was recently obtained for the Cr acceptor binding energy.[5]

Since the 0.56 eV luminescence band always accompanied the appearance of the 0.8 eV band in the bulk samples, this deeper luminescence might also be attributable to chromium, in this case, in the Cr^{3+} state. Photoluminescence experiments on the chromium doped liquid epitaxial layer are consistent with this hypothesis. This sample is *n*-type with a resistivity of $10^4\ \Omega$ cm which indicates incomplete compensation of donors. For incomplete compensation of donors all the chromium is expected to be in the Cr^{2+} state. The 0.8 eV Cr^{2+} luminescence band was observed in this epitaxial sample while the deeper 0.56 eV band was not detected. At present, however, the evidence for the assignment of the observed luminescence bands to Cr^{2+} and Cr^{3+} ions is far from conclusive and this model must be considered as no more than a hypothesis.

Additional experiments are being carried out in which the luminescence results are correlated with optical effects in electron spin resonance measurements on GaAs:Cr[20] in the hope that additional evidence for the assignment of the 0.56 eV luminescence to the Cr^{3+} states will be obtained. The critical experiments to be performed involve controlled doping of the "pure" bulk material with both chromium and a shallow donor (e.g. Sn, Te, Se).

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