

# IDENTIFICATION OF TRANSITION METALS IN GaN

K. PRESSEL\*, R. Heitz\*\*, L. ECKEY\*\*, I. LOA\*\*, P. THURIAN\*\*, A. HOFFMANN\*\*, B.K. MEYER\*\*\*, S. FISCHER\*\*\*\*, C. Wetzel\*\*\*\*, E.E. Haller\*\*\*\*

\*Institut für Halbleiterphysik, P.O. Box 409, 15204 Frankfurt(Oder), Germany

\*\*Inst. für Festkörperphysik, Techn. Univ. Berlin, 10623 Berlin, Germany

\*\*\*Physik-Department E16, Techn. Univ. München, 85748 Garching, Germany

\*\*\*\*Lawrence Berkley Laboratory, Univ. of California, Berkley, CA 94720, U.S.A.

## ABSTRACT

We present a photoluminescence study of residual transition metal contaminants in hexagonal GaN layers. We observe three no-phonon lines peaking at 1.3 eV, 1.19 eV and 1.047 eV. The no-phonon line at 1.3 eV is caused by the internal electronic transition  ${}^4T_1 \rightarrow {}^6A_1$  of  $Fe^{3+}$ . The 1.19 eV emission, which was first attributed to  $Cr^{4+}$ , is caused by  $Ti^{2+}$ . GaN layers intentionally doped with Cr, V, or Ti during growth have been investigated. Only the Ti doped samples show an intense signal of the 1.19 eV emission. The experimental data of the luminescence center at 1.047 eV, which appears as natural contaminant only in GaN layers grown by the sandwich technique, fit best to the  ${}^4T_2(F) \rightarrow {}^4A_2(F)$  transition of  $Co^{2+}$ . The three no-phonon lines show characteristic phonon sidebands. Most of them correspond to phonon modes observed in Raman spectroscopy.

## INTRODUCTION

In recent years the development of an AlGaIn/InGaIn blue green light emitting diode [1] stimulated worldwide the efforts to develop also a GaN based blue green laser. Up to now photoluminescence (PL) measurements on GaN have mainly been performed in the near bandedge region at about 3.4 eV and in the range of the yellow luminescence at around 2.2 eV. Only a few studies have been published hitherto on emissions in the near infrared region (NIR) of GaN [2, 3, 4]. Luminescence centers in the near infrared are caused by internal electronic transitions of 3d elements which are incorporated as natural contaminants during crystal growth. In this paper we focus on three luminescence centers in GaN which show no-phonon (NP) lines peaking at 1.3 eV, 1.19 eV, and 1.047 eV and characteristic phonon replica.

## EXPERIMENTAL

The GaN samples were grown by means of high temperature vapor phase epitaxy (HTVPE) [5] or by a modification of the sandwich technique [6]. Both techniques utilize liquid metallic Ga and  $NH_3$  as precursors. The main characteristics are the small distances between the Ga melt and the substrates ( $\leq 5$  mm) and the high growth temperature around 1200°C. Doping of the GaN with transition metals was done by adding the respective transition metal in a ratio of 1:1000 to the Ga melt. The films were deposited either on (0001) 6H-SiC or (0001) sapphire substrate. The PL measurements were performed using a BOMEM DA8.02 Fourier-spectrometer. The PL excitation (PLE) measurements were performed with conventional monochromator technique. For all the measurements a Ge-detector was used.

## RESIDUAL 3d TRANSITION METALS IN GaN

Figure 1 shows a near infrared PL spectrum of a GaN sample grown by the sandwich technique on 6H-SiC. We observe three NP lines with transition energies at 1.3 eV, 1.19 eV, and 1.047 eV and their corresponding phonon sidebands. In the inset a detailed spectrum of one of the samples in the range of the 1.047 eV emission is depicted. In addition to the 1.047 eV emission, labelled A, further weaker emissions appear which are caused by so far unidentified defects.

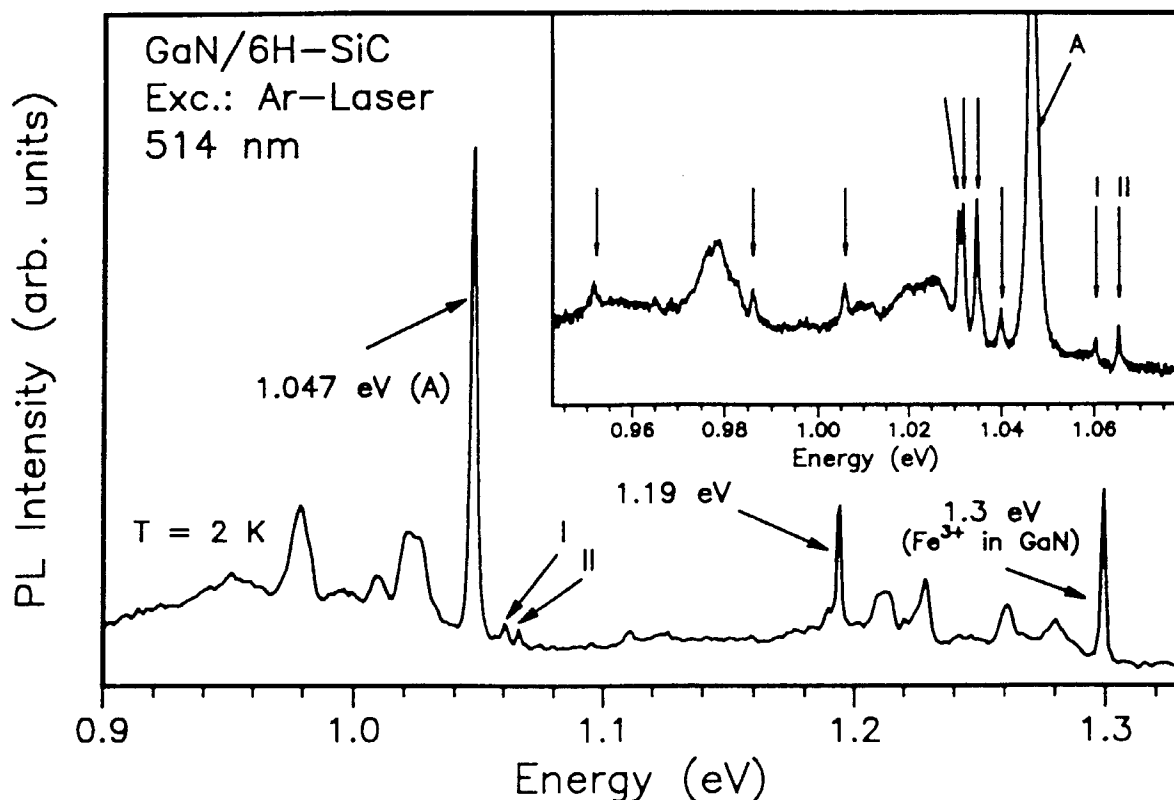


FIG. 1. PL spectrum of GaN/6H-SiC in the near infrared region. Three NP lines peaking at 1.3 eV, 1.19 eV, and 1.047 eV together with GaN related phonon sidebands appear. The inset shows a detailed spectrum of another sample in the range of the 1.047 eV transition. In some of the samples additional luminescence lines indicated by the arrows appear. They are caused by further contaminations and complexes.

The  $\text{Fe}^{3+} \ ^4\text{T}_1 \rightarrow \ ^6\text{A}_1$  in GaN (1.3 eV)

The emission at 1.3 eV was first reported by Maier et al.[2]. Based on EPR-, PL-, and ODMR this emission was assigned to the electronic spin-flip transition between the  $^4\text{T}_1$  excited state and  $^6\text{A}_1$  ground state of  $\text{Fe}^{3+}$ . This attribution has been confirmed using Zeeman spectroscopy showing the typical splitting of the  $^6\text{A}_1$  ground state [11, 12]. However the excitation mechanism of the  $\text{Fe}^{3+}$  luminescence is not established yet. Only in some of our samples we can excite the  $\text{Fe}^{3+}$  emission with the 514 nm green line of the Ar ion laser. Thus, most definitely different defects are involved to excite the  $\text{Fe}^{3+}$  emission. For instance in some samples the luminescence excitation spectrum of the yellow band at 2.2 eV coincides with the excitation spectrum of  $\text{Fe}^{3+}$ . Excitation via the substrate has to be considered as well. Therefore the bandoffsets determined from the  $\text{Fe}^{3+/2+}$  levels by Baur et al. [4] have to be regarded with care.

In PL and absorption measurements we searched for the internal electronic transition of  $\text{Fe}^{2+}$ . In nearly all semiconductor hosts the typical four line pattern of the  $\text{Fe}^{2+}$  transition  $^5\text{T}_2 \rightarrow ^5\text{E}$  is resolved. From their PLE measurements Baur et al. assumed that the  $\text{Fe}^{2+}$  transitions are located at about 0.5 eV [4]. Up to now we were not able to detect any trace of  $\text{Fe}^{2+}$  in the optical range between 0.2 eV and the visible region. In absorption we studied a n-type  $400\mu\text{m}$  sample which showed a strong  $\text{Fe}^{3+}$  emission. Possible explanations are: (a) As already pointed out for  $\text{Fe}^{2+}$  in ZnO [10], where also the  $\text{Fe}^{2+}$  emission is not observed, the large vibrational energy of the optical phonons favour nonradiative relaxation. (b) All our samples are n-type. As shown for  $\text{Fe}^{2+}$  in GaAs and InP the  $\text{Fe}^{2+}$  emission decreases the higher the n-type character of the samples [7].

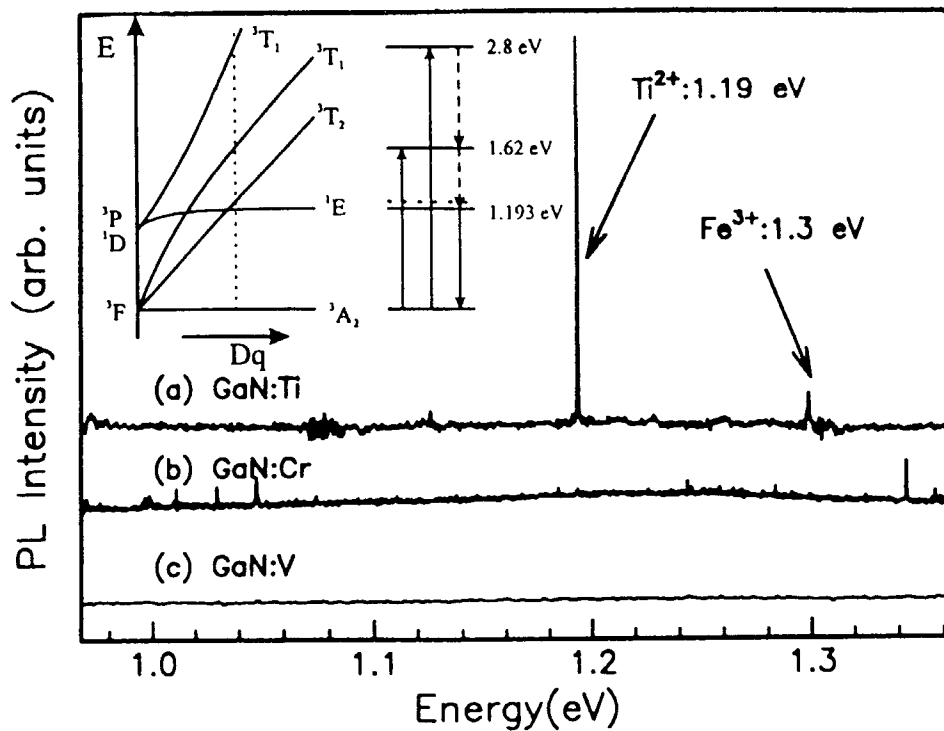


FIG. 2. Near infrared PL spectra of GaN doped with (a) Ti, (b) Cr, and (c) V. Only the Ti doped sample shows the 1.19 eV luminescence center using below and above bandgap excitation. The level scheme explains the observed transitions according to Ref. [12, 13].

The 1.19 eV emission was first reported by Baur et al. in their GaN samples grown on sapphire by VPE or MOVPE [8]. They assigned the luminescence center to  $Cr^{4+}$ . But according to our optical investigations the luminescence center is caused by an internal electronic transition between the  ${}^1E$  and  ${}^3A_2$  levels of  $Ti^{2+}$  (see level scheme of Fig. 2).

In contrast to Baur et al. [8] the temperature-dependent PL studies of all our samples both grown by the sandwich technique and grown by MOVPE or HTVPE show no excited state to the 1.19 eV emission. Zeeman measurements show a three-fold splitting of the ground state of the 1.19 eV emission in GaN. Thus the ground state belongs to a  $S=1$  system. Details on the excitation and Zeeman measurements are published elsewhere [12, 13]. Thus, the luminescence center has a  $3d^2$  electronic configuration. The luminescence center cannot only be excited by above bandgap excitation but also by excitation in the region between 1.5 eV and 1.65 eV. This excitation band is attributed to an absorption into an excited state of our luminescence center. The appearance of the excited state reveals that the defect center is already in its luminescence charge state without illumination in n-type GaN. Possible candidates are  $Ti^{2+}$ ,  $V^{3+}$ , and  $Cr^{4+}$ . We observe the 1.19 eV emission also in our samples where the electronic concentration  $n$  is higher than  $10^{17} \text{ cm}^{-3}$ . Because the emission center is already in its luminescence charge state in the dark an attribution to a 3d element in a 4+ charge state is improbable. Thus we attribute the 1.19 eV emission to the  ${}^1E \rightarrow {}^3A_2$  transition of  $Ti^{2+}$ . This assignment to  $Ti^{2+}$  is confirmed by doping experiments where different transition metals were introduced during crystal growth. Fig. 2 shows three spectra of GaN samples which have been intentionally doped with Ti, V, and Cr during HTVPE growth. Only the Ti-doped GaN sample showed the 1.19 eV emission.

#### The 1.047 eV emission: $d^7$ configuration

The emission at 1.047 eV occurs only in GaN samples grown by the sandwich technique and no identification has been attempted yet.

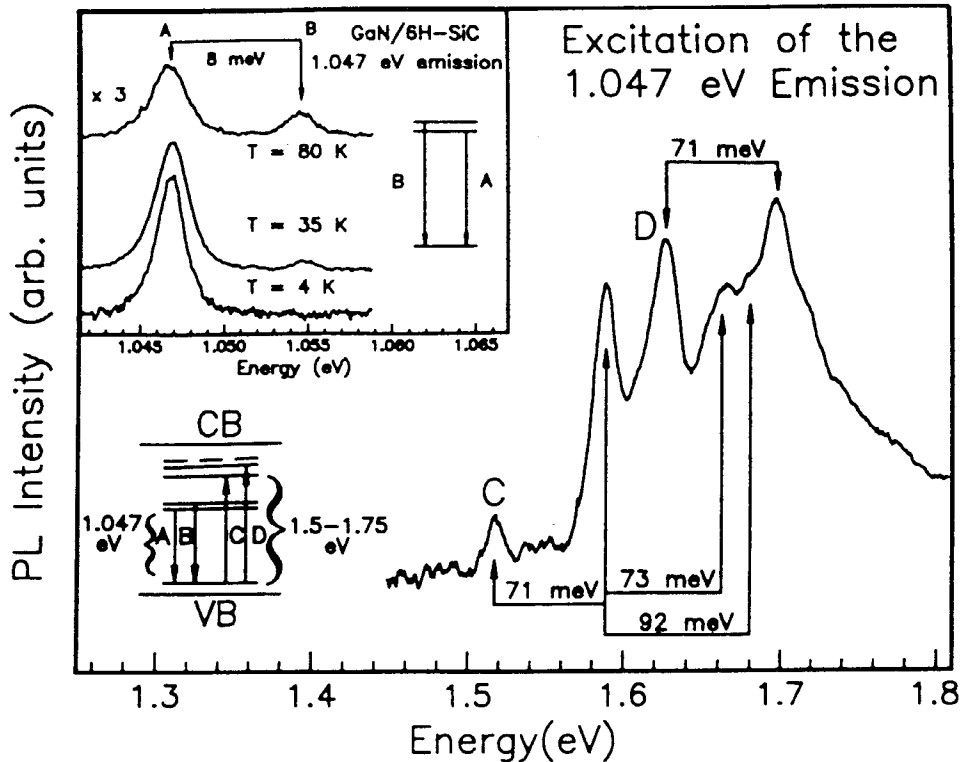


FIG. 3. PL excitation spectrum of the 1.047 eV luminescence center. A set of at least six absorption peaks is detected. The absorptions C and D are caused by NP transitions. The inset shows the appearance of a hot line (B) to the 1.047 eV NP line (A) indicating a splitting of the excited state.

Figure 3 shows an excitation spectrum of the 1.047 eV emission in the optical range between 1.45 and 1.8 eV. Similar to the 1.19 eV emission the 1.047 eV emission can be excited not only by above bandgap excitation but also in the energetic range between 1.5 eV and 1.75 eV. This absorption band consists of a set of at least six sharp peaks. The absorption peaks C and D can be attributed to NP lines. The other peaks coincide with replicas having typical phonon energies of GaN (see also next section)

A charge-transfer transition can most definitely be excluded. As observed for the excitation spectrum of the 1.19 eV emission (Fig. 2) the excitation spectrum of the 1.047 eV emission reveals excitation via an excited state. Therefore the luminescence center is in its luminescence charge state in the dark in n-type material. The inset of Fig. 3 shows three spectra of the 1.047 eV emission detected at different temperatures. With increasing temperature a hot line 8 meV higher in energy appears. Thus we have an at least two-fold split excited state. The scheme in the left part indicates the level scheme derived from the temperature dependent PL measurements and the PLE measurements. We only observe one NP line at 2 K. Thus, the 1.047 eV emission can belong to a 3d transition metal with a  $d^1$ ,  $d^2$ ,  $d^5$ , or  $d^7$  electronic configuration all having an orbital momentum in the ground state.

For the following reasons the 1.047 eV emission is caused by a transition metal with a  $d^7$  electronic configuration: (a) A  $d^1$  configuration can be excluded because it has no excited state that can explain the higher excited state observed in PLE (Fig. 3) (b) In our n-type samples we exclude  $\text{Cr}^{4+}$ .  $\text{Ti}^{2+}$  and  $\text{V}^{3+}$  are already attributed to other emission centers at 1.19 eV [13] and 0.931 eV [8], respectively. Furthermore, the excitation spectrum of the 1.047 eV emission looks different to the excitation spectrum usually observed for  $\text{Ti}^{2+}$  or  $\text{V}^{3+}$ . (c) The  ${}^4T_1 \rightarrow {}^6A_1$  spin-flip transition of a  $3d^5$  configuration can be excluded because the decay time of less than a few  $\mu\text{s}$  is too short.

Therefore the experiments fit to a transition metal with a  $3d^7$  electronic configuration. As  $\text{Fe}^+$  can be excluded as well, the possible candidates are  $\text{Ni}^{2+}$  and  $\text{Co}^{2+}$ . Usually Ni appears as  $\text{Ni}^+$  or  $\text{Ni}^{2+}$  in semiconductors. Therefore the  ${}^4T_2 \rightarrow {}^4A_2$  transition Co in its 2+ charge state is the most probable possibility to cause the 1.047 eV emission.

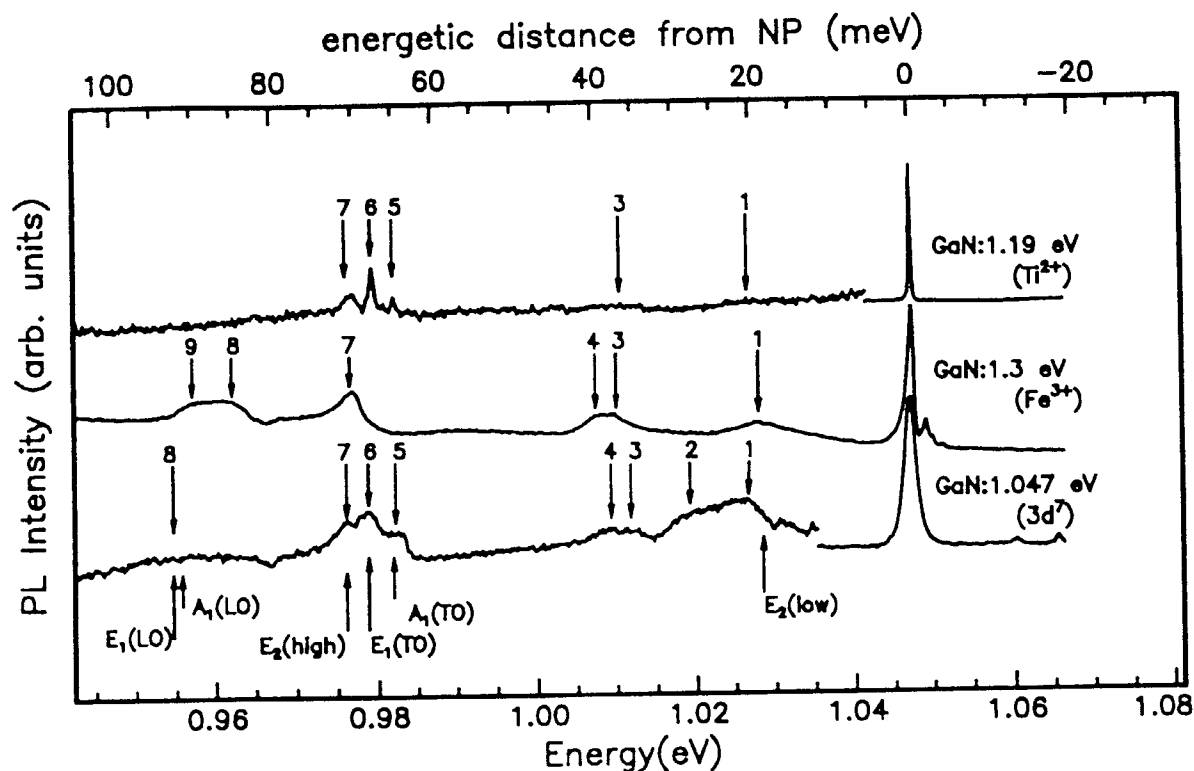


FIG.4 Comparison of the phonon sidebands of the three no-phonon lines caused by residual transition metal contaminants. The emissions are normalized to the 1.047 eV emission. The top scale indicates the distance of the phonon replica from the no-phonon lines. The phonon modes observed from Raman spectroscopy are indicated (see Tab. 1).

Raman modes GaN (Kozawa et al. [14]) cm <sup>-1</sup> /meV	1.047 eV cm <sup>-1</sup> /meV	1.19 eV cm <sup>-1</sup> /meV	1.3 eV (Fe <sup>3+</sup> in GaN) cm <sup>-1</sup> /meV
E <sub>2</sub> (low): 144/17.9	169/21.0 (1) 219.4/27.2 (2) 286.8/35.6 (3) 308.4/38.2 (4)	~ 170/21.1 (1) ~ 295/36.6 (3)	154/19.1 (1) 301/37.3 (3) 316/39.2 (4)
E <sub>2</sub> (high): 570/70.7	569.4/70.6 (7)	569.0/70.5 (7)	569.3/70.6 (7)
A <sub>1</sub> (TO): 532/66	527.8/65.4 (5)	524.8/65.1 (5)	
E <sub>1</sub> (TO): 561/69.6	549.9/68.2 (6)	547/67.8 (6)	
A <sub>1</sub> (LO): 736/91.2	~		690/85.6 (8)
E <sub>1</sub> (LO): 745/92.4	750/93.0 (8)		717/88.9 (9)

TAB. 1. Energies of the phonon replica (determined from Fig. 4) of the three NP lines at 1.047 eV (column 2), 1.19 eV (column 3), and 1.3 eV (column 4). The energies of the phonon modes are given in cm<sup>-1</sup> (for better comparison with Raman data) and in meV. The numbers in brackets indicate the maxima according to Fig. 4. The phonon modes of hexagonal GaN determined from Raman spectroscopy [14] are summarized in the first column.

In Fig. 4 and Tab.1 the phonon sidebands of the three defect luminescence bands and the phonon modes observed from Raman spectroscopy are compared. The phonon modes observed in the phonon sidebands are close to modes observed from Raman spectroscopy [14].

## CONCLUSIONS

In a nutshell, we studied residual transition metal contaminants in GaN samples grown on 6H-SiC and on sapphire substrate. By photoluminescence we observe three no-phonon lines peaking at 1.3 eV, 1.19 eV, and 1.047 eV. Our Zeeman measurements support the attribution of the 1.3 eV emission to the  ${}^4T_1 \rightarrow {}^6A_1$  transition of  $Fe^{3+}$ . On the basis of Zeeman studies, photoluminescence excitation spectroscopy, and intentional doping experiments, the 1.19 eV emission is attributed to the  ${}^1E \rightarrow {}^3A_2$  transition of  $Ti^{2+}$ . The 1.047 eV emission is probably caused by an internal electronic transition of a transition metal with a  $3d^7$  electronic configuration. Our experimental data at best fit to the  ${}^4T_2 \rightarrow {}^4A_1$  of  $Co^{2+}$ . The phonon sidebands of the three luminescence centers show resonances close to the phonon modes observed in Raman spectroscopy

## ACKNOWLEDGEMENT

The support of the Deutsche Forschungsgemeinschaft DFG is gratefully acknowledged. One of the authors, K. Pressel, is indebted to the *Stifterverband der Deutschen Wissenschaft* for financial support to visit the MRS meeting on *GaN and Related Materials*.

## References

- [1] S. Nakamura, T. Mukai, and M. Senoh, *J. Appl. Phys.* **76**, 8189 (1994)
- [2] K. Maier, M. Kunzer, U. Kaufmann, J. Schneider, B. Monemar, I. Akasaki, and H. Amano, in *Material Science Forum 143-147, Defects in Semiconductors 17*, edited by H. Heinrich and W. Jantsch (Trans Tech Publications, Aedermannsdorf, Switzerland, 1994) p. 93
- [3] J. Baur, K. Maier, M. Kunzer, U. Kaufmann, J. Schneider, H. Amano, I. Akasaki, T. Detchprohm, and K. Hiramatsu, *Appl. Phys. Lett.* **64**, 857 (1994)
- [4] J. Baur, K. Maier, M. Kunzer, U. Kaufmann, and J. Schneider, *Appl. Phys. Lett.* **65**, 2211 (1994)
- [5] S. Fischer, C. Wetzel, E. Bourret, W.L. Hansen, and E.E. Haller, presented at the 1995 MRS spring meeting, San Francisco (unpublished)
- [6] C. Wetzel, D. Volm, B.K. Meyer, K. Pressel, S. Nilsson, E.N. Mokhov, and P.G. Baranov, *Appl. Phys. Lett.* **65**, 1033 (1994)
- [7] S.G. Bishop, in *Deep Centers in Semiconductors*, edited by S. Pantelides (Gordon & Breach, New York, 1986), p. 541
- [8] J. Baur, U. Kaufmann, M. Kunzer, J. Schneider, H. Amano, I. Akasaki, T. Detchprohm, and K. Hiramatsu, *Appl. Phys. Lett.* (1995)
- [9] B. Clerjoud, C. Naud, B. Deveaud, B. Lambert, B. Plot, G. Bremond, C. Benjeddou, G. Guillot, and A. Nouailhat, *J. Appl. Phys.* **58**, 4207 (1985)
- [10] L. Podlowski, R. Heitz, P. Thurian, A. Hoffmann, I. Broser, *J. of Lumin.* **58**, 252 (1994)
- [11] R. Heitz, P. Thurian, I. Loa, L. Eckey, A. Hoffmann, I. Broser, K. Pressel, B.K. Meyer, E.N. Mokhov, accepted for publication in *Appl. Phys. Lett.*
- [12] R. Heitz, P. Thurian, A. Hoffmann, K. Pressel, to be published in *Proc. of the 18th International Conference on Defects in Semiconductors*, Sendai, Japan
- [13] R. Heitz, K. Pressel, P. Thurian, I. Loa, L. Eckey, A. Hoffmann, I. Broser, B.K. Meyer, E.N. Mokhov, accepted for publication in *Phys. Rev. B*
- [14] T. Kozawa, T. Kachi, H. Kano, Y. Taga, M. Hashimoto, N. Koide, and K. Manabe, *J. Appl. Phys.* **75**, 1098 (1994)