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# INTERNAL RADIATIVE TRANSITIONS ON THE SECOND AND THIRD TRANSITION SERIES IONS IN GaAs AND GaP

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Photoluminescence due to II and III transition series elements (Zr, Nb, Mo, Pd, W) is observed for the first time in GaAs and GaP and interpreted on the basis of Tanabe-Sugano diagrams. The contribution of optical transitions with the change of spin is emphasized. The role of electron-phonon interaction in forming phonon-assisted photoluminescence and in broadening and shift of zero-phonon lines is studied.

## I. Introduction

When considering the scheme of levels of "optical" d-electrons of transition elements in crystal matrixes it should be born in mind, that electron-electron interaction (characterised by Racah parameters A, B, C) decreases while crystal field (parameter Dq) increases as one passes from the first to the second and third transition series [1]. In consequence, in the latter two cases the energy and the succession of electronic states belonging to various atomic terms differ from those for the first (iron) series. It means in particular, that radiative transitions between states with different spins can be observed in semiconductors even with moderate band gap. The examples of such transitions can be found in photoluminescence (PL) spectra of GaAs and GaP doped by II and III transition series elements (TSE), which are presented for the first time in this paper. To introduce Zr, Nb, Mo, Pd and W into crystals we used ion implantation technique, which proved to be a very effective means of doping the semiconductors by transition elements [2,3].

## II. Photoluminescence Spectra

PL spectrum of GaAs:W (Fig.1) consists of narrow zero-phonon lines (ZPL) at 707, 702 and 678 meV and relatively broad phonon-assisted line (PAL) at 651 meV. In the temperature range 4.2 - 20 K width of the most intense ZPL 678 meV does not exceed 0.17 meV and that of weaker ZPL 1 meV, the latter being resolution-limited. For GaAs:Nb and GaP:Nb ZPL are at 796 and 759 meV respectively, their widths at 4.2 - 20 K being close to those for GaAs:W. PAL in PL spectrum of GaAs:Nb are separated from ZPL by energies 11, 23, 27, 32 and 55 meV. In the case of GaP:Nb only one PAL was observed at 43 meV from ZPL. The PL of GaAs:W was detectable up to the room temperature, in the GaAs:Nb and GaP:Nb - up to $T \simeq 150$ K and $\simeq 220$ K respectively. So we can conclude, that in GaAs:Nb,W and GaP:Nb PL is due to internal optical transitions, both (excited and ground) states lying within the gap. In all

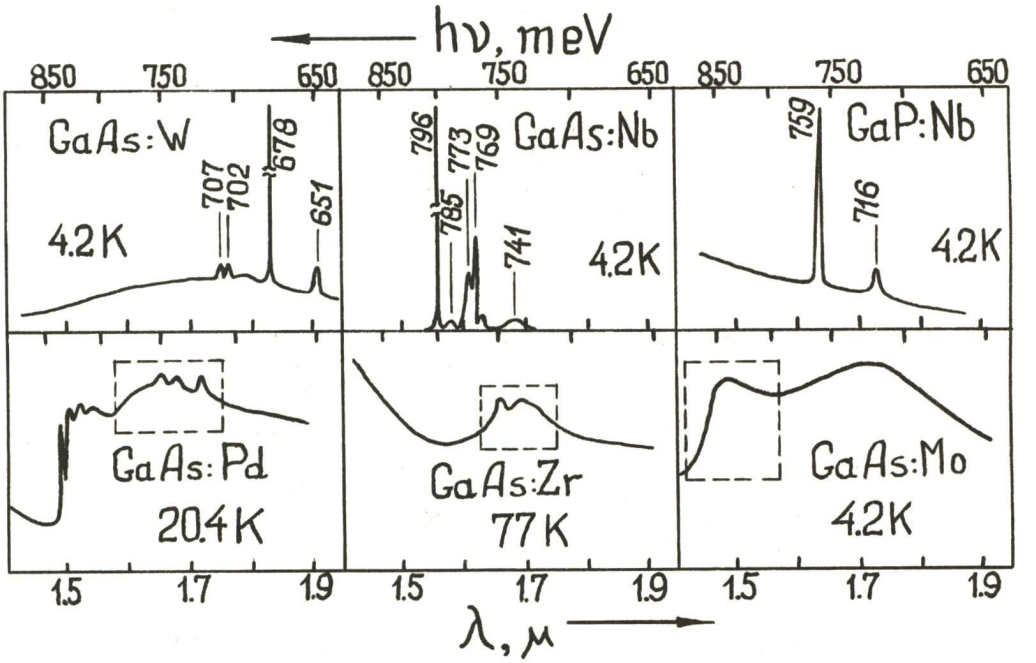


Fig. 1 Photoluminescence spectra

three cases the whole spectrum is shifted to the lower energies with the increase of temperature. PL of GaAs:Zr,Mo,Pd is represented by weak lines and bands superimposed on the spectrum of the initial (undoped but annealed) material.

## III. Electronic Transitions

The PL of II and III TSE is observed in crystals with various initial (prior to implantation) electron concentration. Its intensity tends to increase when the latter is of the order of implanted impurity concentration. It suggests that the PL is due to transitions on $A^{-1}$ - centres of TSE with electronic configuration $Me^{2+}$.

The identification of the electronic transitions is based upon Tanabe-Sugano (TS) diagrams [4] for the weak crystal field. This approximation is justified by the following arguments. For the I TSE in III-V compounds Dq is about 400 - 500 $cm^{-1}$. Parameters B and C/B are, respectively, about 400 $cm^{-1}$ and 4.3 [5]. Thus for the I TSE Dq/B 1.0-1.2 and weak field condition is satisfied. The observed structure of PL of GaAs:W, which is due to spin-orbit splitting of the ground state, can only be explained in terms of weak field, since for the strong field the ground state is singlet. So we see, that even for III TSE (5d-electrons) weak field approximation is valid (but of course for strong interaction between levels).

The electron-phonon coupling in the PL of GaAs:Nb,W is weak (Fig.1), which is characteristic of optical transitions between states with different spins [1]. Then it should be noted that ZPL of GaP:Nb is shifted to lower energies relative to that of GaAs:Nb,

while Dq in GaP is somewhat higher than in GaAs (according to data on I TSE). This is an indication, that the upper state of the transition on Nb centre is represented by a descending branch of TS-Diagram. The transition $^2T_1$ - $^4T_1$ (Fig.2) complies with these facts. In this case $B \simeq 350$ cm$^{-1}$. It is difficult to determine the value of Dq because of weak dependence of the energy of the transition $^2T_1$ - $^4T_1$ on crystal field strength. As a preliminary estimate the ratio Dq/B for the II TSE can be taken as intermediate between the values for I TSE (1.0-1.2) and III TSE (the boundary of weak field region, i.e. 2.2), which makes $Dq/B \simeq 1.6$.

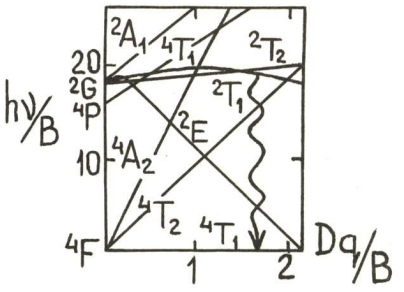


Fig.2 TS-diagrams for $d^3$-electrons

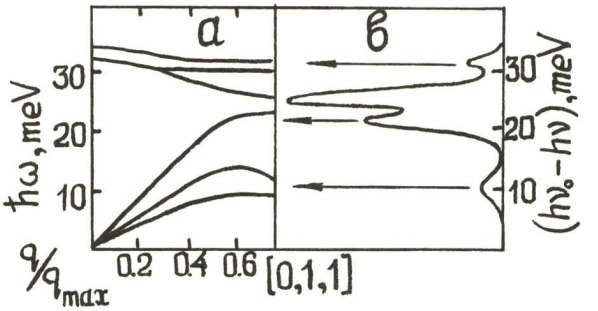


Fig. 3 GaAs phonon dispersion curves(a), and PAL structure of GaAs:Nb(b)

Basing upon similar arguments, it can be suggested, that weak, but narrow lines in PL spectra of GaAs:Pd and possibly, GaAs:Zr, also arise from the transitions with the change of spin $^1T_2(^1E)$ - $^3T_1(^3A_2)$ while the broad PL band of GaAs:Mo is due to the transition $^5E$ - $^5T_2$ (observed also in GaAs:Cr [6,7]).

The interpretation of PL spectrum of GaAs:W presents some difficulties due to the uncertainty in the value of B. Assuming that the value of B for III TSE does not differ drastically from those cited for I and II TSE, since it depends not only on properties of d-electrons but largely on the covalence of the material, it can be suggested that PL of GaAs:W is due to either $^1T_1$ - $^5T_2$ or $^3T_2$ - $^5T_2$ transitions.

## IV. Electron-Phonon Interaction

Phonon-assisted lines in our PL spectra are due to interaction of electronic transitions with phonons, whose wavevectors are close to the boundary of Brillouin zone. For example, the comparison of PL structure of GaAs:Nb with phonon dispersion curves [8] (Fig.3) shows, that this electronic transition interacts with [0,0.7,0.7] - phonons. The "selectivity" of the interaction probably indicates that the symmetry of the centre is different from that of tetrahedron (Jahn-Teller effect).

Electron-phonon interaction manifests itself also as broadening and shift of ZPL. The latter are very narrow at low temperatures in GaAs:W,Nb and GaP:Nb ($\simeq$0.16 meV at 4.2 K). ZPL in GaAs:W at 4.2 K is symmetrical (gaussian). With the increase of T it broadens, at first (up to $\simeq$ 20 K) somewhat asymmetrically. At 77 K

its shape is close to lorenzian and at ≃ 200 K - again to gaussian. The ZPL in GaAs:Nb at 4.2 K is asymmetrical. This asymmetry (which is of nonthermal origin at this temperature and not due to isotopical effects, since we used single isotope implantation) may be caused not only by local strains in the lattice, but also by tunnel splitting of ZPL, since all centres considered are of Jahn-Teller type. At 20 - 30 K ZPL of GaAs:Nb becomes symmetrical, then at higher temperature asymmetry appears, but of the opposite sign relative to that observed at 4.2 K.

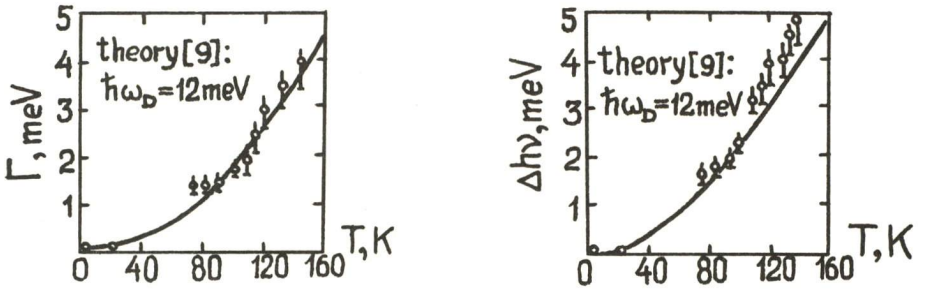


Fig.4 Broadening $\Gamma$ and shift $\Delta h\nu$ of ZPL of GaAs:Nb

The shift $\Delta h\nu$ and broadening $\Gamma$ of ZPL in GaAs:W,Nb and GaP:Nb, characteristic of anharmonic centres in crystal lattice, are in agreement with the theory [9], according to which $\Delta h\nu$ and $\Gamma$ are due to second-power terms in the electron-phonon interaction operator and can be treated as Raman scattering of phonons on impurities (PAL are due to linear terms of the same operator). If the spectrum of phonons which effectively interact with the optical transitions is approximated by the Debye function, then the theoretical curve $\Gamma(T)$ can be fitted to the experimental data for GaAs:Nb,W and GaP:Nb with $\hbar\omega_D$= 10 ÷ 15 meV (Fig.4). The difference between coupling constant for these centres does not exceed factor two. Similarly, the shift $\Delta h\nu(T)$ for ZPL of GaAs,GaP:Nb is satisfactorily given by the theory. So we may conclude that it is the interaction with acoustical phonons that gives the main contribution to the broadening and shift of the observed ZPL.

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