Phonon replicas of recombination radiation of an electron–hole liquid in ZnO

L. F. Gudymenko, E. G. Gule, M. P. Lisitsa, and A. M. Yaremko

Semiconductor Institute, Ukrainian Academy of Sciences
(Submitted 20 July 1978; resubmitted 18 September 1978)
Pis'ma Zh. Eksp. Teor. Fiz. **28**, No. 8, 509–511 (20 October 1978)

The temperature dependence of recombination radiation of ZnO single crystals is investigated at high excitation levels. The *2LO* and *3LO* phonon replicas of the emission band of an electron–hole liquid were observed for the first time in the temperature interval 4.2–70 K.

PACS numbers: 71.35. + z, 78.55.Hx

It is known that the recombination radiation of ZnO single crystals at 4.2 K consists of lines of free and bound excitons and of their phonon replicas.[1] At 77 K only the lines of the free excitons and of their phonon replicas remain in the spectrum.[2–4]

At high excitation levels and at 4.2 K, an electron-hole plasma band is superimposed on the bound-exciton line. It is of interest to investigate the temperature dependence of the luminescence spectrum of ZnO at such excitation levels. The results may yield the temperature intervals in which different recombination channels manifest themselves.

The recombination radiation spectra of ZnO single crystals (see Fig. 1) were obtained with a PGS-2 spectrograph following excitation with an LGI-21 nitrogen laser. The frequencies (energies) of the bound excitons are labeled symbol I, and those of the free excitons A and B_T. As seen from Fig. 1, the luminescence spectrum at 4.2 K is determined by the I–mLO phonon replicas of the bound exciton. They practically vanish when the temperature is raised to 50 K, while the phonon replica bands B_T–LO and A–$2LO$ of the free excitons, which are hardly noticeable at 4.2 K, become more intense.

The electron-hole plasma emission at 4.2 K is concentrated in the spectral region 369–369.5 nm. If the emission of sufficiently pure sections of the samples is investigated, then an excitation level that ensures a carrier density $\sim 10^{18}$ cm^{-3} produces in the recombination radiation spectrum a band whose emission maximum at 4.2 K is located at 369.5 nm (on the low-energy side of the lines of the bound exciton I). With increasing temperature this band shifts towards lower energies. The temperature dependence of this shift is represented by the upper curve in the insert of Fig. 1. The spectral position at 4.2 K and the temperature interval (up to 70 K) in which this band exists make it possible to identify this band with the emission band of direct recombination of an electron-hole liquid.[5] As seen from Fig. 1, the temperature dependence of the position of the recombination-radiation band of an electron-hole liquid differs from that for indirect band-gap semiconductors, for example silicon.[6] The reason is that in direct band-gap semiconductors the existence of the electron-hole liquid is due to strong e–h phonon interaction.[7,8] In accordance with Ref. 7, the energy decrease for

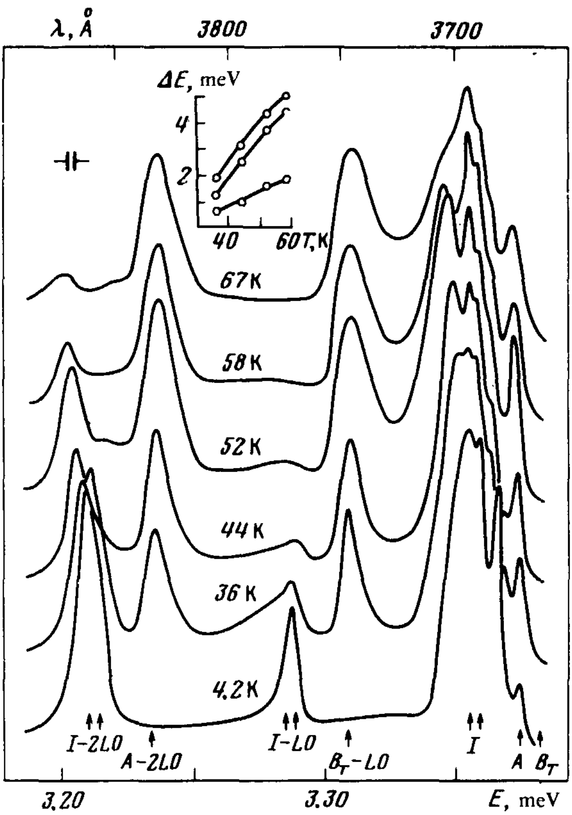

FIG. 1. Dependence of the recombination radiation spectra of ZnO on the temperature. Insert: temperature shift of the recombination radiation band of the electron-hole liquid and of its $2LO$ phonon replica (upper and middle curves, respectively) and shift of the exciton bands (lower curve). (The shift ΔE is relative to arbitrarily fixed points on the energy scale.)

electron-hole liquids in semiconductors with ionic bond at relatively low carrier densities is due to the polaron effects. With increasing density of the electron-hole liquid, the polaron contribution weakens somewhat. Therefore when the temperature is raised, in accordance with the phase diagram,[9] the density of the electron-hole liquid decreases, the binding energy of the electron-hole liquid should increase in accordance with Ref. 7, and the energy of the recombination-radiation quantum decreases, as is in fact observed in experiment.

Particular interest attaches to the band that appears at $T\sim 10$–20 K on the long-wave edge of the band of the I–$2LO$ phonon replica of the bound exciton (3.2094 eV). With increasing temperature it shifts towards lower energies (see Fig. 1) and vanishes at 70 K. Judging from its temperature dependence (middle curve of the insert in Fig. 1) this band cannot be interpreted as the result of interaction of the bound exciton with the LO phonons (the temperature shift of the exciton band is shown by the lower curve of the insert). Its temperature shift correlates only with the behavior of the band identified above with the electron-hole liquid emission. In the entire temperature interval in which the described band and the recombination radiation band of the electron-hole exists, the distance between them is constant at 144 meV and is equal to the energy of two LO phonons. The temperature at which it vanishes (70 K) corresponds to the critical temperature of the electron-hole liquid in ZnO single crystals.[5]

All this suggests that this band is a 2–*LO* phonon replica of the recombination radiation of the electron-hole liquid.

We note that no 1–*LO* phonon replica of the recombination radiation band of the electron-hole liquid is observed. This fact agrees well with the results of Ref. 10, where it was shown that in pure crystals the 1–*LO* phonon replica of the exciton radiation or of the recombination radiation of an electron-hole pair is weak, and its intensity becomes discernible only in crystals containing enough impurities.

We note in conclusion that a band whose behavior with changing temperature is quite analogous to the one just described is observed also on the long-wave edge of the 3–*LO* phonon replica band of the bound exciton. This allows us to regard it as a 3–*LO* phonon replica of the recombination radiation of the electron-hole liquid. The intensity of the last band, just as the intensity of the 3–*LO* phonon replicas of the bands of the free and bound excitons, is much lower than that of the 1–*LO* and 2–*LO* bands.

[1]C. Klingshirn, Phys. Status Solidi B **71**, 547 (1975).
[2]R.L. Weiher and W.C. Tait, Phys. Rev. **166**, 791 (1968).
[3]A. Kh. Abduev, A.D. Adukov, B.M. Ataev, R.A. Rabadanov, and D.A. Shaikhov, Kvantovaya Elektron. (Moscow) **5**, 206 (1978) [Sov. J. Quantum Electron. **8**, 126 (1978)].
[4]I. Filinski and T. Scettrup, Solid State Commun. **6**, 233 (1968).
[5]I. Scettrup, Solid State Commun. **23**, 741 (1977).
[6]Jagdeep Shah, M. Combescot, and A.H. Davem, Phys. Rev. Lett. **38**, 1497 (1977).
[7]G. Beni and T.M. Rice, Phys. Rev. Lett. **37**, 874 (1976).
[8]L.V. Keldysh and A.P. Silin, Zh. Eksp. Teor. Fiz. **69**, 1053 (1975) [Sov. Phys. JETP **42**, 535 (1975)].
[9]R.F. Leheny and Jagdeep Shah, Phys. Rev. Lett. **38**, 511 (1977).
[10]A.A. Gogolin and E.I. Rashba, Solid State Commun. **19**, 1177 (1976).