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Comments

Comments are short papers which criticize or correct papers of other authors previously published in the **Physical Review**. *Each Comment should state clearly to which paper it refers and must be accompanied by a brief abstract. The same publication schedule as for regular articles is followed, and page proofs are sent to authors.*

Comment on "Radiative and nonradiative recombination of bound excitons in GaP:N. I. Temperature behavior of zero-phonon line and phonon sidebands of bound excitons" and " Radiative and nonradiative recombination of bound excitons in GaP:N. IV. Formation of phonon sidebands of bound excitons"

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We point out that the experimental data on the temperature dependence of the LO-phonon sidebands of NN_{4-6} in a recent paper by X. Zhang *et al.* [Phys. Rev. B **41**, 1376 (1990)] are incorrectly analyzed, and that the theory in a closely related paper by Q. Hong, X. Zhang, and K. Dou [Phys. Rev. B **41**, 2931 (1990)] is inadequate for explaining the LO-phonon sideband structure and temperature behavior of N-related bound excitons in GaP.

In a recent series of papers Zhang *et al.*[1] (hereinafter referred to as XZ) report previously obtained experimental results[2] on the anomalous temperature behavior of the phonon sidebands (PS) of NN_i bound excitons (BE) in GaP:N. In a related paper[3] they present a theory of "two components" to explain these results as well as the double-peak structure of LO PS in NN_i BE spectra. In this Comment we point out that neither the anomalous experimental results nor the theory which purports to account for those results is valid.

The BE of NN_i in GaP have been extensively studied since the 1960s. The PS associated with the bulk modes as LO^Γ, X, TO^Γ, LA, and TA have been measured since the beginning of this study.[4] They belong to both isolated N and to NN_i pair centers, and have been used in measurements of lifetime[5] and of the thermal quenching,[6] on the assumption that the PS follow their no-phonon (NP) line's behavior. Up to now, there has not been any inconsistency between experimental results and this understanding, except for the work of XZ. According to the measurements of XZ, the ratio of the LO PS tc their corresponding NP line is strongly temperature dependent for some NN_i (but not for the deeper NN_1 and NN_3) pair centers, varying from about 0.5 at low temperature to as much as 15–25 at around 50 K for NN_4, NN_5, and NN_6. Within the CC (configurational coordinate) model, these results imply an anomalously strong temperature dependence of the Huang-Rhys parameter S, as in the CC model the intensity ratio of the first PS to the NP line equals S. XZ first proposed a model of "exciton-LO phonon complex"[2] to account for this anomalous temperature dependence. Subsequently they withdrew this model and substituted a new "two-component" (TC) model.[1,3] In the TC model, the double peak (i.e., LO^Γ and X) structure of LO PS was interpreted as one peak (LO^Γ) being due to the CC transition and the other (X) due to a MC (momentum-conserving) transition, and the anomalous temperature behavior of the LO PS comes from the MC component.

XZ complained[1] that "the different temperature behavior between no-phonon lines and phonon sidebands has not yet received much attention." This is incorrect. There have been thorough studies[7,8] on this subject after XZ's first report,[2] but they are ignored in XZ's recent papers.[1,3] High-resolution measurements of the temperature variation of the photoluminescence (PL) spectra with both nonselective[7] and selective excitation[8] have clearly shown that the "anomalous" temperature dependence of LO PS reported in Ref. 2 was due to erroneous assignment of the PS. The error arose because of overlap ("mixing" was used for "overlap" in Refs. 7 and 8) between the optical PS of $NN_{4,5,6}$ and the acoustic PS of NN_3.[9] The results of Refs. 7 and 8 show that, contrary to XZ's claim,[2] the PS-to-NP ratio and hence the Huang-Rhys parameter S is independent of temperature. Very recent work[10] on GaAs:N has also reached the same conclusion. Explicitly, when the LO PS of NN_i ($i = 4–6$) are carefully followed,[7] they gradually disappear with increasing temperature, due to the fact that the shallower centers NN_4–NN_6 quench faster than the deeper center

NN$_3$, as shown in Fig. 3 of Ref. 7. Thermally activated energy transfer from the shallower centers to the deeper ones further enhances the PL intensity from the NN$_3$ center. The TA and LA PS of NN$_3$ were mistaken for the LO PS of NN$_4$–NN$_6$ by XZ, leading to an apparently "anomalous" temperature behavior of the latter. When the intensity ratio of the NN$_3$ TA or LA PS to a NP line of the shallower centers (NN$_4$–NN$_6$) was plotted against temperature, a very similar result to that of "LO PS" to their NP lines of NN$_4$–NN$_6$ reported by XZ in Refs. 2 and 1 was obtained.[7] It is thus not surprising that XZ reported[1,2] that the activation energy for thermal quenching of NN$_3$, NN$_3$-LO, "NN$_4$-LO," "NN$_5$-LO," and "NN$_6$-LO" have almost the same value, as they all actually correspond to the same thermal quenching process of the NN$_3$ center, since at higher temperatures the PL of NN$_3$ took over that of the shallower ones. Further, and even more decisively, selective excitation experiments[8] have successfully resolved the PS from different NN$_i$ centers, which overlap each other if above-band-gap excitation is used. Figures 2 and 3 in Ref. 8 show, respectively, the selective excitation spectra at 15 and 54 K where the "anomaly" reported by XZ is a maximum. These figures confirm that the analysis in Ref. 7 is correct.

The relations between CC and MC models, and XZ's TC model, are thoroughly discussed in a planned paper.[11] A simple argument shows that the TC model could not possibly explain an anomalous temperature behavior of LO PS of NN$_i$ even if it did occur. According to the TC model, the LO$^\Gamma$ peak is still a normal CC transition which has a temperature-independent S parameter. Therefore, any unusual temperature dependence of the LO PS has to be due to a strong temperature dependence of the X peak which is assigned to a MC transition. Whether such a strong temperature dependence is possible or not, we just check the consequences of only one component having an anomalous temperature behavior. XZ reported in Fig. 2(a) of Ref. 2(b) that the intensity ratio of the LO (LO$^\Gamma+X$) PS to NP line reached a value of 3.5 for NN$_4$ at 37.5 K. At low temperature the total intensity of the LO PS, i.e., LO$^\Gamma$ plus X, is less than 50% of the NP line and the intensity of the two peaks is almost the same; thus if the ratio between LO$^\Gamma$ and NP is kept the same, the value of 3.5 suggests that at 37.5 K the intensity of the X peak should be about 14 times stronger than that of the LO$^\Gamma$ one. Therefore, at 37.5 K the LO PS would not look like a good double-peak band any more and the peak position would shift to that of the X peak. However Fig. 1(a) of Ref. 2(b) shows that at 37.5 K the LO PS of both NN$_3$ and NN$_4$ are still doublets and the relative intensity between their two peaks remains almost the same as that at low temperature. The two-peak structured LO PS of NN$_4$ is apparently superposed on top of the LA PS of NN$_3$. Based on the same argument, if the intensity ratio of LO PS to NP of NN$_4$ reached 13 as reported by XZ, the intensity of the X peak would be about 60 times stronger than that of the LO$^\Gamma$ one. However, Fig. 3 of Ref. 8 shows that even at 54 K the LO PS of NN$_4$ is still a doublet (in contrast to XZ's unresolvable LO spectra in this temperature region which are apparently due to the overlap of LA PS of NN$_3$), and the relative intensity between its two peaks again remains unchanged from that at low temperature. At higher temperatures still, where the two peaks are not well resolved, the relative intensity between them seems to remain unchanged since the peak shifts to a position intermediate between the LO$^\Gamma$ and X peaks.[7]

In conclusion, this Comment shows that, as was already known at the time Ref. 1 of XZ was submitted, the temperature behavior of the LO PS of NN$_i$ in GaP is not in fact anomalous; furthermore, their two-component model does not even explain their own results. The double-peak feature of the LO PS of NN$_i$ has been an unsolved problem for a long time, and various models have been proposed to account for it. In Ref. 11 we plan to deal with this subject.

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[9] Possible confusion induced by the overlap of PS's from different NN$_i$ centers was warned about at an early stage of the study of GaP:N, e.g., in Ref. 6 by Sturge, Cohen, and Rogers.

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