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# COUPLING OF NITROGEN-BOUND EXCITONS WITH PHONONS IN GaP:N*

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ABSTRACT

In this paper, the technique of photoluminescence was used to study the coupling between nitrogen-bound excitons and phonons in GaP:N in the temperature region 15—80 K. Several samples with different nitrogen concentrations were adopted. The results of the study show that the zero-phonon line and each relevant one-phonon line from one $NN_i$ center have the same temperature dependence, this is consistent with the Huang-Rhys' multiphonon light transition theory. Every one of the S factors is independent of temperature.

## I. INTRODUCTION

Isoelectronic impurity N can introduce a series of bound exciton states in GaP:N material. These states are associated with an exciton bound to an isolated N site or an N—N pair with different spacings. Usually the zero-phonon emission lines arising from the radiative recombination of the bound excitons were labeled as A or $NN_i$ ($i = 1, 2, \cdots, 10$) in the spectrum[1]. Owing to the fact that the potential of the isoelectronic traps are strongly localized, the bound excitons may quite uniformly couple over the whole range of phonon wave vectors in the Brillouin zone. Thus, besides the zero-phonon line, various phonon sidebands would appear in the emission spectrum.

From the study on temperature-variational photoluminescence in GaP:N, H. Chang et al.[2] have found that the thermal quenching law of the $LO^{\Gamma}$ phonon sideband is fully different from that of the zero-phonon line for the $NN_i$ centers; the ratio of their integrated intensities depends on the temperature strongly and the ratio could vary with temperature in two orders of magnitude. Meanwhile they also obtained the same results for $GaAs_{1-x}P_x$:N and $Ga_xIn_{1-x}P$:N at some compositions. W. Zhang et al[3]. also observed a similar phenomenon in GaP:N. Such phenomenon contradicts the well-knoun multiphonon light transition theory. Since this theory was advanced by K. Huang and A. Rhys[4] and S. Y. Pekhar[5] separately in 1950, it has found wide applications to various fields of solid spectral

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work[6,7]. It also has been used in the investigations of the bound exciton luminescence produced by isoelectronic centers in III-V compound semiconductors[8,9]. According to the theory, the strength of the electron-phonon coupling may be expressed by a temperature-independent parameter $S$, known as the Huang-Rhys factor. But the above-mentioned results have shown that one could not get a temperature-independent $S$ factor in GaP:N. It is worthwhile investigating the problem further.

In this work, the temperature-variational photoluminescence in GaP:N samples with different nitrogen doping levels have been studied in the range of 15—80K. By means of tracing identification of the concerned spectral lines with changing temperature and making some calculations, we have observed that, for all $NN_i$ center, the $LO^\Gamma$ phonon sideband has the same temperature relation as the zero-phonon line in the temperature region considered. For every one of the phonon sidebands, a temperature-independent $S$ factor can be determined.

## II. Experimental Considerations

The experimental system for this work is shown schematically in Fig. 1. Samples were set in the sample cell of CSA-202E refrigerator. Both the temperature control and indication are within the accuracy of $\pm 0.5$ K. An YJ-3 $Ar^+$ laser was used as the excitation source, of which the power measured was about 4 mW[10] and mainly at 4880Å. The excitation power was monitored and its fluctuation was within 5% through the experiment. The laser beam modulated by a chopper was focused on the sample with a diameter of nearly 0.2 mm by using a lens. The illumination sport was imaged onto the entrance slit plane of a GDM-1000 grating double monochrometer. After being dispersed, the luminescence was detected by cooled C31034 photomultiplier and PAR124A lock-in amplifier, then recorded by a recorder. The spectral resolving ability was about 1 $cm^{-1}$.

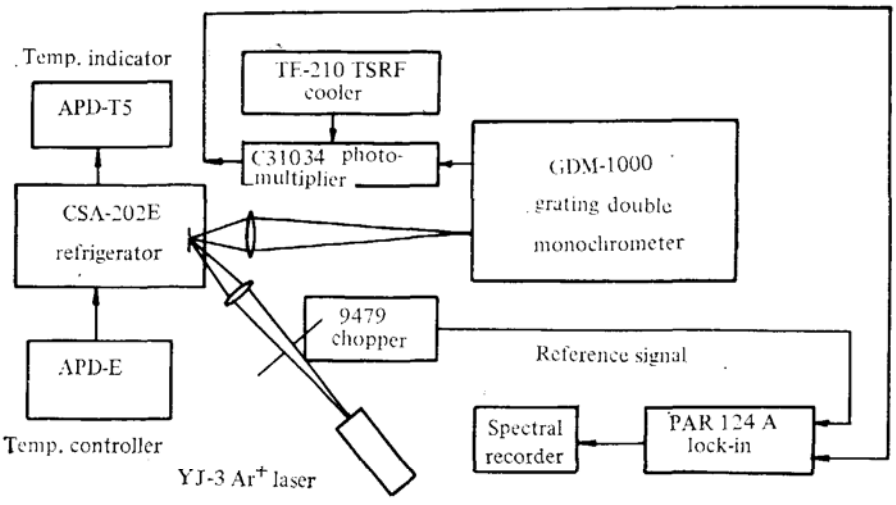


Fig. 1. Block diagram of experiment system for low-temperature photoluminescence.

In the experiment, we adopted three samples with different nitrogen concen-

trations, $2.0 \times 10^{18}\,cm^{-3}$ for HG-1, $2.4 \times 10^{18}\,cm^{-3}$ for SG-1 and $1.0 \times 10^{19} cm^{-3}$ for $G_1$-Y. The concentrations were determined with the optical absorption method[11].

The calibrations of spectral response were carried out for all the spectra and calculations in this paper. The calibration method was to make a total calibration for the total system with a standard lamp whose colour temperature was known.

## III. Experimental Results and Analyses

### 1. *Identification of Spectral Lines*

Fig. 2 is a low-temperature photoluminescence spectrum of GaP:N with low

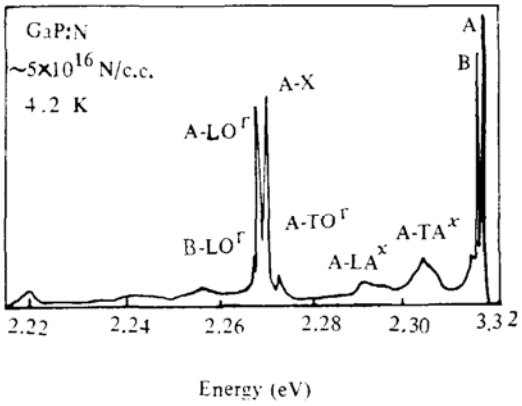


**Fig. 2. The photoluminescence spectrum of excitons bound to isolated N traps[11].**

nitrogen concentration given by Ref. [1]. The spectral lines were produced by excitons bound to isolated N sites. Fig. 3 shows the photoluminescence spectra of sample SG-1 at different temperatures, the phonon sidebands were marked according to the phonon energies published in some references. The values of the phonon energies we have obtained are listed in Table 1, which are in quite good agreement with those presented by Ref. [1, 9, 13, 14]. From Figs. 2 and 3, we can see that the spectral structure of certain $NN_i$ center is much the same as that of the isolated N center, besides the $LO^\Gamma$, $TA^X$, $LA^X$, $TO^\Gamma$ phonon sidebands, another spectral line A-X or $NN_i$-X appears at the energy position 14 $cm^{-1}$ higher than the $LO^\Gamma$ sideband for all of them. The origin of this line is still unclear for the time being. We have labeled the doublet ($NN_i$-$LO^\Gamma$ and $NN_i$-X) as $NN_i^*$ and the correspondent $S$ factor as $S^*$. Also we have observed the phonon sideband corresponding to the local model for $NN_1$ and $NN_3$ centers.

**Table 1**

Phonon Energies in GaP:N (Unit: meV)

| Phonon | $LO^\Gamma$ | $TA^X$ | $LA^X$ | $TO^\Gamma$ | X | $LOC_1$ | $LOC_3$ |
|---|---|---|---|---|---|---|---|
| Energy | 50.1±0.1 | 13.3±0.2 | 26.7±0.4 | 45.4±0.1 | 48.4±0.1 | 61.2±0.2 | 61.5±0.1 |

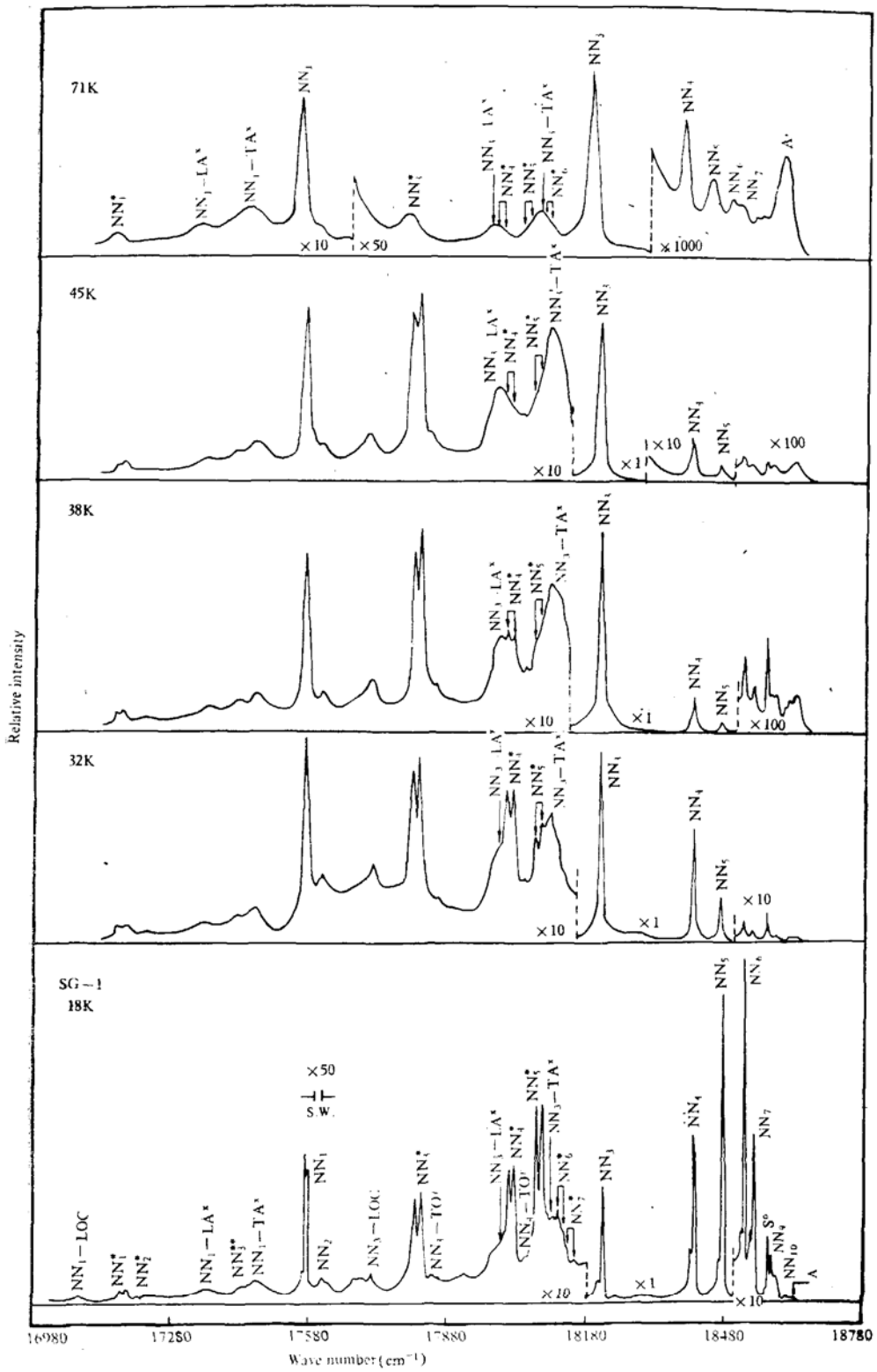


Fig. 3. Photoluminescence spectra of sample SG-1 at different temperatures.

## 2. Analyses and Calculations

According to the multiphonon light transition theory[12], the probability of light transition between initial and final electronic states accompanied by the emission of $p$ phonons of energy $\hbar w$ is given by

$$F_p = |M_{ij}|^2 \left(\frac{\bar{n}+1}{\bar{n}}\right)^{p/2} e^{-S(2\bar{n}+1)} I_p(2S\sqrt{\bar{n}(\bar{n}+1)}), \tag{1}$$

where $I_p$ is a Bessel function of order $p$ and imaginary argument, $\bar{n}$ is the statistic average phonon numbers, $\bar{n} = 1/(e^{\hbar w/kT} - 1)$, $S$ is the so-called Huang-Rhys factor.

For the case of $S^2\bar{n}(\bar{n}+1) \ll 1$, that is, for weaker coupling and lower temperatures, Expression (1) may be simplified as

$$F_p \propto e^{-g} g^p / p! \tag{2}$$

where $g = S(1+\bar{n})$, thus the intensity ratio of the one-phonon line to the zero-phonon line becomes

$$R = g = S(1+\bar{n}). \tag{3}$$

If $\bar{n} \ll 1$, we have $R \approx S$, then ratio $R$ is almost a temperature-independent quantity. In the concerned temperature range ($T < 80$ K), $\bar{n}_{LO^\Gamma} < 10^{-3}$, it was unnecessary to consider the variation of $\bar{n}$ for $LO^\Gamma$ phonon, but this factor must be considered for $TA^X$ and $LA^X$ phonons.

According to the results in earlier investigations, the $S_i^*$ for $i = 4, 5, 6$ could change with temperature in two orders of magnitude, and reach a maximum at about 50 K, their values could exceed 20. Our analyses and calculations show that such an abnormal temperature dependence on $S_4^*$, $S_5^*$ and $S_6^*$ is caused by improper identification of the spectra. One can see from Fig. 3, many spectral lines including $NN_4^*$, $NN_5^*$, $NN_6^*$, $NN_3$-$TA^X$, $NN_3$-$LA^X$, etc. lie within a region of 250 $cm^{-1}$ below the $NN_3$, the intervals between them are less then 20 $cm^{-1}$ for some of them, being easily mixed up. At low temperatures, $NN_4$, $NN_5$ and $NN_6$ are stronger, so $NN_4^*$, $NN_5^*$ and $NN_6^*$ are also stronger and the total integrated intensity in the spectral region of our concern is mainly determined by them. With increasing temperature, the intensities of $NN_4$, $NN_5$ and $NN_6$ quench quickly, the intensity of $NN_3$ does not quench but increases rapidly due to exciton transfer from shallower centers to it[3], and the intensities of $NN_3$-$TA^X$ and $NN_3$-$LA^X$ also increase. So the total integrated intensity in this region is gradually dominated by the $TA^X$ and $LA^X$ phonon sidebands of $NN_3$. While temperature is somewhat higher ($T > 50$ K), the intensities of $NN_4^*$, $NN_5^*$ and $NN_6^*$ are negligible as compared with that of the $NN_3$-$TA^X$ and $NN_3$-$LA^X$. As a result of severe temperature broadening of spectral lines, the intensities at the positions corresponding to $NN_4^*$, $NN_5^*$ and $NN_6^*$ are contributed by the $NN_3$—$TA^X$ and $NN_3$—$LA^X$ practically when the intensities of $NN_4$, $NN_5$ and $NN_6$ are very weak. In this case, it is difficult to separate out the proportions corresponding to $NN_4^*$, $NN_5^*$ and $NN_6^*$. In fact the maxima of $S_4^*$, $S_5^*$

and $S_6^*$ shown in Ref. [12] are relative to the process in which the intensity of $NN_3$ goes up due to exciton-accepting transfer and falls down due to its thermal quenching, also to the contributions of rapid decrease in $NN_4$, $NN_5$ and $NN_6$ intensities with increasing temperature. We have made a calculation on the ratio of $NN_3$—$LA^X$ line to the zero-phonon line of $NN_4$. The ratio exhibited a maximum at about 55 K with a value about 22. This was just consistent with the results in Ref. [2]. Otherwise, we can also pay attention to the results in Refs. [2, 3], where $NN_3$, $NN_3^*$, $NN_4^*$, $NN_5^*$ and $NN_6^*$ almost possess the same value of thermal activation energies and preexponential factors. According to the identification and analyses for the spectra we have made above, such results just reflect the thermal quenching law of $NN_3$ center. It only proves that the zero-phonon line of $NN_3$ has the same temperature relation with its one-phonon sidebands.

Figs. 4—6 show the results of $S_1^*$, $S_1^{TA^X}$, $S_1^{LA^X}$ and $S_3^*$ at different temperatures for three samples. Within the experimental and calculating errors, these parameters are independent of temperature. Table 2 summarizes the $S$ factors corresponding to various phonon sidebands for each $NN_i$ center in the three samples. $S_4^*$, $S_5^*$ and $S_6^*$ were derived from low temperature spectra ($T < 20$ K), $S_3^{TA^X}$ and $S_3^{LA^X}$ were derived from the spectra at higher temperatures ($T > 70$ K).

In the range of $20\text{ K} < T < 70\text{ K}$, for the spectral region referred to above, the spectral line overlapping due to the thermal broadening made it difficult to get those $S$ factors directly. We have calculated the total intensity $\Phi(T)$ in the region at different temperatures. On the basis of the above identification for the spectra, $\Phi(T)$ includes $NN_i^*$ ($i = 4$—$7$) and $NN_3$—$TA^X$, $NN_3$—$LA^X$, that is

$$\Phi(T) = I_4^* + I_5^* + I_6^* + I_7^* + I_3^{TA^X} + I_3^{LA^X}.$$

In the mean time, we are able to give $\Phi'(T)$, here

$$\Phi'(T) = I_4^0 \cdot S_4^* + I_5^0 \cdot S_5^* + I_6^0 \cdot S_6^* + I_7^0 \cdot S_7^* + I_3^0 \cdot S_3^{TA^X} \cdot (1 + \bar{n}_{TA^X}) + I_3^0 \cdot S_3^{LA^X} \cdot (1 + \bar{n}_{LA^X}),$$

where $I_i^0$ represents the zero-phonon line intesity of $NN_i$ center. Theoretically, the

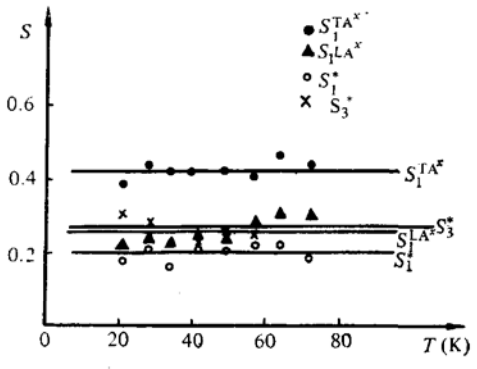


Fig. 4. The $S \sim T$ relations of $NN_1$, $NN_3$ in sample HG-1.

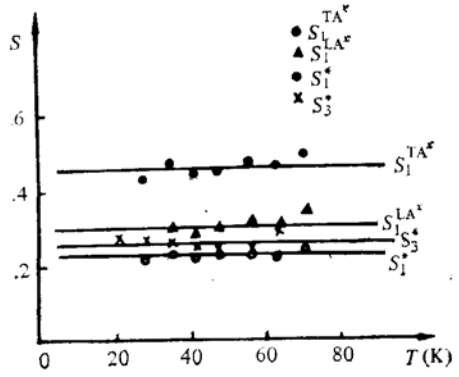


Fig. 5. The $S \sim T$ relations of $NN_1$, $NN_3$ in sample SG-1.

ratio $K = \Phi'/\Phi$ is always equal to 1 at any temperature. We have got the values of $K$ at various temperatures for the three samples as shown in Fig. 7. We can think $K = 1$ within the errors. Such a result means that our identification for the spectra is reliable and the various $S$ factors do not vary with temperature.

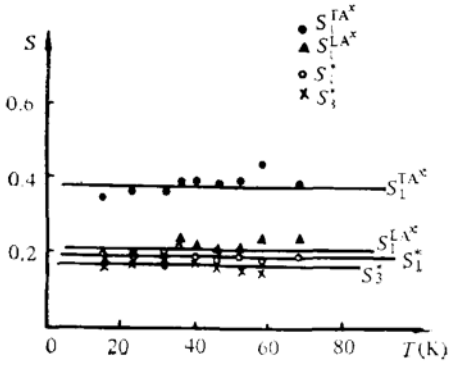


Fig. 6. The $S\sim T$ relations of $NN_1$, $NN_3$ in sample $G_1$—Y.

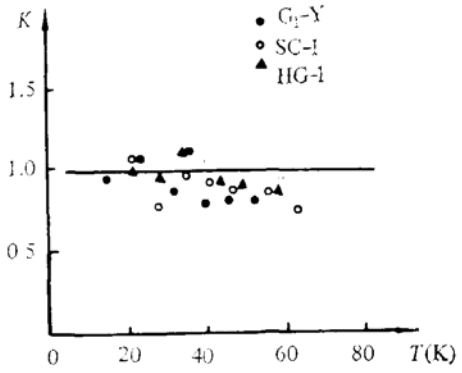


Fig. 7. The $K\sim T$ relations in samples HG-1, GS-1 and $G_1$-Y.

**Table 2**

Huang-Rhys Factors in GaP:N

| Sample \ S | $S_1^*$ | $S_1^{TA^X}$ | $S_1^{LA^X}$ | $S_1^{LOC}$ | $S_3^*$ | $S_3^{TA^X}$ | $S_3^{AL^X}$ | $S_3^{LOC}$ | $S_4^*$ | $S_5^*$ |
|---|---|---|---|---|---|---|---|---|---|---|
| HG-1 | 0.20 | 0.42 | 0.26 | 0.03 | 0.27 | 0.33 | 0.26 | 0.03 | 0.29 | 0.27 |
| SG-1 | 0.23 | 0.46 | 0.30 | 0.04 | 0.26 | 0.37 | 0.27 | 0.03 | 0.29 | 0.29 |
| $G_1$-Y | 0.19 | 0.38 | 0.21 | 0.03 | 0.17 | 0.31 | 0.21 | 0.02 | 0.29 | 0.31 |

Migliorato et al[13] and Wolford et al[8] had proposed that the transitions assisted by large-momentum phonons, e.g. $TA^X$ and local model, would get stronger with respect to the zero-phonon line for increasing nitrogen concentration. They explained such a phenomenon as a delocalization of the wave function in real space. One can see from Table 2 that each $S$ factor we have obtained are independent of nitrogen concentration on the whole. The enhancement on the phonon sidebands of $NN_1$ center observed by them is more likely due to impurity effect.

## IV. Conclusions

From above analyses and calculations, three conclusions can be drawn.

(1) In GaP:N, the coupling between bound excitons and phonons is weaker. For all $NN_i$ centers, their $S$ factors are smaller than 0.5. The coupling strength of bound excitons with a certain kind of phonon does not vary seriously from one center to another.

(2) There are similar spectral structures for all $NN_i$ centers. The emission spectrum for each $NN_i$ center is mainly composed of the zero-phonon line, $LO^\Gamma$,

$TA^X$, $LA^X$ phonon sidebands and $NN_i$—X band.

(3) The zero-phonon line has a same temperature relation with correspondent one-phonon sidebands, which is consistent with the Huang-Rhys multiphonon light transition theory. The various $S$ factors we obtained are independent of temperature.

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## REFERENCES

[1] Thomas, D. G. & Hopfield. J. J., *Phys. Rev.*, **150** (1966), 680.
[2] Zhang Hsinyi, et al., *Sci. Sin.* **125**(1982), 942.
[3] 张渭滨、郑健生，发光与显示，**5**(1984), 8.
[4] Huang, K., *Rhys, A., Proc. Roy. Soc.*, **A204** (1950), 406.
[5] Пекар, С. И., *ЖЭТФ*, **20** (1950), 510.
[6] Pryce, M. H. L., *Phonons in Perfect Lattice and in Lattice with Point Imperfections*, Oliver & Boyd, Edinburgh, 1966.
[7] Stoneham, A. M., *Theory of Defects in Solid*, Clarendon Press, Oxford, 1975.
[8] Wolford, D. J., et al., *Solid State Commun.*, **19** (1976) 741.
[9] Евстротов, В. В., *ФТЛ*, **10** (1976), 1898.
[10] 郑健生，物理学报，**29**(1980), 286.
[11] 颜炳章、郑健生，厦门大学学报(自然科学版)，1981, 2:195.
[12] 黄 昆，物理学进展，**1**(1981), 31.
[13] Migliorato, P. et al., *Solid State Commun.*, **14**(1974), 893.
[14] Dean, P. J. et al., *Phys. Rev.*, **B4**(1971), 1926.