PHYSICAL REVIEW B VOLUME 46, NUMBER 23 15 DECEMBER 1992-I

Resonant scattering of exciton polaritons in ZnP_2 crystals

Osamu Arimoto, Hideki Takeuchi, and Kaizo Nakamura
Department of Physics, Okayama University, Okayama 700, Japan

(Received 17 August 1992)

Secondary emission of monoclinic zinc diphosphide is investigated under excitation into the exciton resonance region at 2 K. Distinct emission lines are observed in the vicinity of the 1*s* exciton energy, shifted from the excitation energy by the longitudinal-optical (LO) phonon energies. It is shown that these lines are caused by inelastic scattering of exciton polaritons by the LO phonons with nearly equal energies of 32.2 and 31.3 meV. The LO lines show the so-called "outgoing resonance"; the lines are enhanced resonantly as they approach the energy of a transverse or longitudinal exciton. The observed phonon energies are related to the exciton damping constants derived from temperature dependence of the reflection spectra. It is concluded that among numbers of phonons, the LO phonons of 32 meV govern the relaxation processes of exciton polaritons in ZnP_2.

Monoclinic zinc diphosphide is one of the II-V compound semiconductors with the space group C_{2h}^5, which contains eight formula units in a unit cell.[1] In spite of this complex crystal structure, it has a very clear hydrogenlike exciton series in the absorption and reflection spectra. For the polarization $E \| c$, pronounced reflection structures due to a direct allowed exciton are observed near 800 nm.[2-10] For the $E \| b$ polarization, absorption lines due to a triplet exciton are weakly observed because of the small spin-orbit interaction.[2,3,5,7,11] Pevtsov *et al.* have found the exciton series up to $n = 7$ in the absorption spectrum for the 1.2-mm-thick crystal.[2] Recently the formation of excitonic molecules has been reported under high-density excitation.[12-14]

As for the lattice vibration, there are 72 phonon modes in monoclinic ZnP_2 since it contains eight molecules per unit cell. Of these, 33 modes are infrared active and 36 modes are Raman active. So far, several modes of infrared-active phonons have been identified from infrared reflection spectra.[15,16] However, there have been no reports on the ordinary nor resonant Raman scattering, probably due to the weak exciton-phonon interaction.

Recently, semiconductor lasers have been available as an intense monochromatic light source in the near-infrared region. In the present work we have undertaken an experiment to observe the resonant Raman scattering of monoclinic ZnP_2 under excitation into the exciton resonance region, by using a semiconductor laser. From comparison with the infrared spectra, we have identified resonant one-LO-phonon scattering lines with energies $\hbar\omega_{\mathrm{LO}} = 32.2$ and 31.3 meV.

Single crystals of monoclinic ZnP_2 were grown from the vapor phase, as described in the previous papers.[9,10] The obtained crystal contains an optically flat surface of the *bc* plane. Experiments were performed on this plane. The experimental configuration was a backscattering geometry with the polarization of incident and scattered light both parallel to the *c* axis $a'(c,c)\bar{a}'$. Here the a' denotes the direction normal to the *bc* plane.[17] The incident light source was a $Ga_{1-x}Al_xAs$-type semiconductor laser (~777 nm, 5 mW). The lasing wavelength was changed around 777 nm by about 3 nm, by controlling temperature of the laser element through the Peltier effect. The incident light was passed through a filter monochromator and focused onto the sample. Emission was analyzed by a 50-cm single monochromator and a cooled photomultiplier (HTV R1477) with a usual lock-in detection system. The band pass of the analyzing monochromator was 0.4 meV.

Figure 1 shows a series of emission spectra around the 1*s* exciton energy under excitation with various energies,

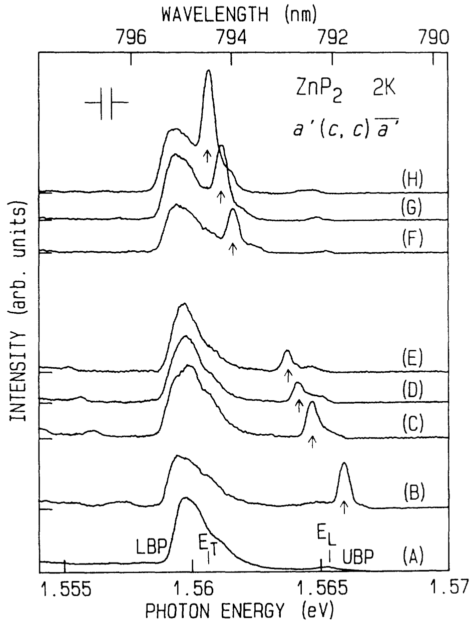

FIG. 1. Secondary-emission spectra obtained at 2 K under various excitation energies, 1.5982 eV (*B*) to 1.5931 eV (*H*). For reference, the emission spectrum obtained under band-to-band excitation with a He-Ne laser is shown by the curve (*A*). E_T and E_L represent positions of the transverse and the longitudinal exciton energies, respectively. As for the experimental configuration, see the text.

1.5982 eV (B) to 1.5931 eV (H). These photon energies fall into the region of the $2s$ to $3s$ exciton resonances. For reference, emission spectrum induced under band-to-band excitation with a He-Ne laser (6328 A, 1 mW) is shown by the curve (A). The E_T and E_L in the figure represent positions of the transverse and longitudinal energies of the $1s$ exciton.[10] In the case of interband excitation (A), there appear emission bands from the lower branch polariton (LBP) and the upper branch polariton (UBP) at E_T and E_L, respectively.[4,6,9] In the case of resonant excitation (B) to (H), new emission lines indicated by arrows appear in addition to the ordinary polariton luminescence. Their energy positions change with excitation energies. The energy shift from excitation energy is $\Delta E = 32.2 \pm 0.1$ meV.

Sobotta *et al.* measured infrared reflection spectra of monoclinic $\mathrm{ZnP_2}$.[15] They obtained frequencies of 14 transverse-optical (TO) vibration modes, as well as associated longitudinal-optical (LO) modes, by an analysis of the spectra with the Kramers-Kronig method. The energy shift of emission lines $\Delta E = 32.2$ meV is close to the energy of the LO phonon 31.9 meV (257 $\mathrm{cm^{-1}}$), which is associated with the most pronounced reflection structure for the polarization $E \perp b$.[15] Therefore the observed emission lines can be attributed to one-LO resonant Raman scattering or one-LO hot luminescence, which appears as a result of the Fröhlich interaction between excitons and Raman-forbidden LO phonons.

Figure 2 shows secondary-emission spectra obtained under resonant excitation at various tempertures. As temperature is raised, luminescence from lower branch polaritons decreases and luminescence from upper branch polaritons increases, both shifting to the lower-energy side. On the other hand, the one-LO line keeps its position and decreases in intensity with increasing temperature to disappear around 50 K, where the polariton luminescence still remains.

In ZnTe, one-LO and two-LO scattering lines appear around exciton resonance at high temperatures (~100 K).[18] In CdS and InAs, furthermore, resonant LO-phonon scattering lines are observed even at room temperature.[19,20] These are in contrast with the present result. It is supposed that interaction between excitons and LO phonons is not so strong in $\mathrm{ZnP_2}$ as compared with that in other II-VI or III-V compounds.

It is seen in curves (B) to (H) of Fig. 1 that the one-LO scattering line is accompanied by a small structure at slightly higher energy. The structure was recognized more distinctly for another sample, as shown in Fig. 3. A scattering line marked by closed circles, which is shifted from incident light by 31.3 ± 0.1 meV, appears at higher energy of the one-LO scattering line marked by arrows. According to the analysis of infrared spectra, the energy of the TO phonon associated with the LO phonon of 31.9 meV is 29.6 meV.[15] Therefore this line is not due to the TO phonon but possibly due to another LO phonon. It is probable that two closely located LO phonons ($\hbar\omega_{\mathrm{LO}} = 32.2$ and 31.3 meV) appear in the present emission spectra, which are not resolved in the infrared lattice vibration spectra.[15] In addition to these LO-phonon lines, several small scattering lines are found, as shown by vertical bars in the figure. Some of these lines are related to the infrared-active phonons.[15]

It is seen in Figs. 1 and 3 that these two one-LO lines

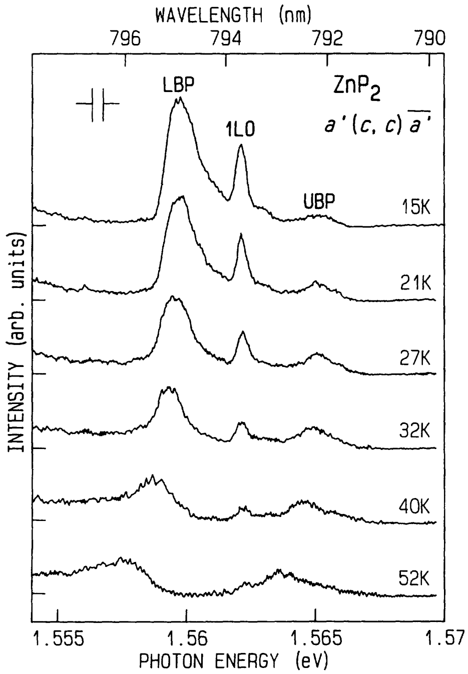

FIG. 2. Secondary-emission spectra obtained under resonant excitation at various temperatures.

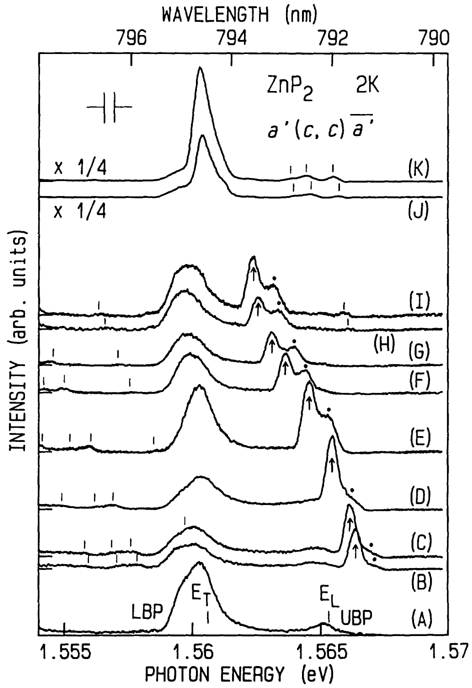

FIG. 3. Secondary-emission spectra obtained at 2 K under various excitation energies, 1.5986 eV (B) to 1.5922 eV (K). For reference, the emission spectrum obtained under band-to-band excitation with a He-Ne laser is shown by the curve (A).

are strongly enhanced as the scattered photon energies approach the resonance energy of the 1s exciton E_T. Namely, they show *outgoing resonance*.[21] For the secondary-emission processes in which the final energy falls into the resonant region, the polariton scattering efficiency is given mainly by the factor T_f/V_f.[22] Here T_f is the transmission coefficient defined by the ratio of the emitted photon flux to the polariton flux inside the crystal, and V_f is the group velocity of final polariton states. It is considered that the observed enhancement of the scattering efficiency is caused by a sharp decrease of V_f, namely by the increase of the final density of states of the lower branch around E_T.[22]

A resonance enhancement also occurs at longitudinal exciton energy E_L. The high efficiency of this scattering process may be connected with the high transmission coefficient T_f of the lower branch at the energy E_L,[6] or with the high density of states at the bottom of the upper branch.

In the case of resonant excitation, the luminescence from the upper branch polariton is very weak or almost vanished at low temperature, as compared with the case of band-to-band excitation, as seen in Figs. 1 and 3. This can be ascribed to the difference in the relaxation processes of exciton polaritons. In the case of interband excitation, polaritons relax by the successive scatterings of LO and acoustic phonons down to around the energy $E_T+\hbar\omega_{\mathrm{LO}}$ in the lower branch, followed by multiple scatterings of acoustic phonons. After attaining quasithermal equilibrium around the bottleneck and also around the bottom of the upper branch, polaritons escape from the sample as the ordinary luminescence. In the case of resonant excitation, on the other hand, the one-LO scattering process is the most dominant relaxation path. Consequently polaritons escape from the sample as the scattering light or hot luminescence before the thermal equilibrium, so that the polariton luminescence from the upper branch becomes weak at low temperature. It should be noted that the upper branch luminescence increases in intensity with increasing temperature, as seen in Fig. 2, which indicates that thermalization due to acoustic phonons proceeds at higher temperature.

As described above, there appear several scattering lines under the resonant excitation, as shown in Fig. 3 by arrows, closed circles, and vertical bars. Of these, the one-LO scattering line shown by arrows with $\hbar\omega_{\mathrm{LO}}=32.2$ meV is the most intense. This fact indicates that the exciton polariton interacts effectively with this mode of phonon. In order to confirm this, we reexamine the temperature dependence of the exciton damping constant obtained in the previous study,[10] where the reflection spectra of the 1s exciton were measured at various temperatures and analyzed based on the exciton polariton model proposed by Hopfield and Thomas.[23] In the numerical calculation, the damping constant Γ above E_T was assumed to be proportional to the energy, owing to the interaction of the exciton with acoustic phonons,[24,25]

$$\hbar\Gamma=\begin{cases}\alpha & (E\le E_T)\\ \alpha+\beta(E-E_T)/E_{\mathrm{LT}} & (E>E_T)\ ,\end{cases} \tag{1}$$

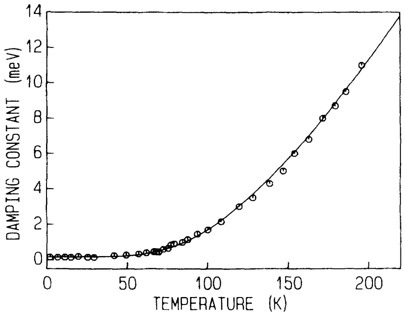

FIG. 4. Temperature dependence of the damping constant of the exciton polariton, obtained by the analysis of reflection spectra at various temperatures. The solid curve represents the theoretical curve calculated by taking $\hbar\omega_{\mathrm{LO}}=32.2$ meV as a LO-phonon energy.

where E_{LT} is energy of the longitudinal-transverse splitting of the 1s exciton, E_L-E_T. In Fig. 4, the damping constant α obtained from the analysis of reflection spectra is plotted as a function of temperature. The solid curve represents the calculated curve obtained by assuming the following formula as the damping constant:[26]

$$\Gamma(T)=\Gamma_0+AT+Bn_{\mathrm{LO}}(T)\ . \tag{2}$$

The first term on the right-hand side denotes a temperature-independent damping constant. The second term arises from exciton interactions with acoustic phonons. The last term arises from interactions with LO phonons and is proportional to the Bose function $n_{\mathrm{LO}}(T)$ for LO-phonon occupation,

$$n_{\mathrm{LO}}(T)=\frac{1}{\exp(\hbar\omega_{\mathrm{LO}}/kT)-1}\ , \tag{3}$$

where $\hbar\omega_{\mathrm{LO}}$ is a LO-phonon energy. The solid curve was drawn by taking $\hbar\omega_{\mathrm{LO}}=32.2$ meV as a LO-phonon energy. The curve well reproduces the temperature dependence of the damping constant. The LO-phonon energy $\hbar\omega_{\mathrm{LO}}=31.3$ meV gives almost the same results. It is therefore considered that among numbers of phonons the exciton polaritons are coupled dominantly to these modes of LO phonons with energies of ~32 meV.

In summary, we have identified LO-phonon lines either by resonant Raman scattering or by the hot luminescence process in monoclinic $\mathrm{ZnP_2}$ under excitation into the 2s to 3s exciton resonances. Two closely located LO-phonon lines are resolved in the scattering spectra with energies of 32.2 and 31.3 meV. The LO scattering lines show *outgoing resonance* enhancement both at E_T and E_L of the 1s exciton. The intensity of luminescence from the upper branch polariton is relatively weak under the resonant excitation, as compared with that obtained under the interband excitation. This can be attributed to the difference of exciton relaxation processes for both excitations. It is concluded that, though the interaction is weak, the LO phonons of 32 meV govern the relaxation processes of exciton polaritons in $\mathrm{ZnP_2}$ crystal.

[1] M. E. Fleet and T. A. Mowles, Acta Crystallogr. C **40**, 1778 (1984).

[2] A. B. Pevtsov, S. A. Permogorov, A. V. Sel'kin, N. N. Syrbu, and A. G. Umanets, Fiz. Tekh. Poluprovodn. **16**, 1399 (1982) [Sov. Phys. Semicond. **16**, 897 (1982)].

[3] N. N. Syrbu and V. M. Mamaev, Fiz. Tekh. Poluprovodn. **17**, 694 (1983) [Sov. Phys. Semicond. **17**, 433 (1983)].

[4] R. S. Berg, P. Y. Yu, and T. Mowles, Solid State Commun. **46**, 101 (1983).

[5] V. V. Sobolev and A. I. Kozlov, Phys. Status Solidi B **126**, K59 (1984).

[6] A. B. Pevtsov, A. V. Sel'kin, N. N. Syrbu, and A. G. Umanets, Zh. Eksp. Teor. Fiz. **89**, 1155 (1985) [Sov. Phys. JETP **62**, 665 (1985)].

[7] N. N. Syrbu, S. B. Khachaturova, and S. I. Radautsan, Dokl. Akad. Nauk SSSR **286**, 345 (1986) [Sov. Phys. Dokl. **31**, 53 (1986)].

[8] V. V. Sobolev, A. I. Kozlov, Yu. I. Polygalov, V. E. Tupitsyn, and A. S. Poplavnoi, Phys. Status Solidi B **154**, 377 (1989).

[9] O. Arimoto, S. Okamoto, and K. Nakamura, J. Phys. Soc. Jpn. **59**, 3490 (1990).

[10] O. Arimoto, M. Tachiki, and K. Nakamura, J. Phys. Soc. Jpn. **60**, 4351 (1991).

[11] S. Taguchi, T. Goto, M. Takeyama, and G. Kido, J. Phys. Soc. Jpn. **57**, 3256 (1988).

[12] N. M. Belyi, I. S. Gorban', V. A. Gubanov, and I. N. Dmitruk, Pis'ma Zh. Eksp. Teor. Fiz. **50**, 75 (1989) [JETP Lett. **50**, 85 (1989)].

[13] T. Goto and Y. Goto, J. Lumin. **48/49**, 103 (1991).

[14] T. Goto and Y. Goto, J. Phys. Soc. Jpn. **60**, 1763 (1991).

[15] H. Sobotta, H. Neumann, N. N. Syrbu, and V. Riede, Phys. Status Solidi B **115**, K55 (1983).

[16] N. N. Syrbu and S. B. Khachaturova, Fiz. Tverd. Tela (Leningrad) **27**, 2687 (1985) [Sov. Phys. Solid State **27**, 1611 (1985)].

[17] The *a* axis is not normal to the *bc* plane in monoclinic ZnP_2. The angle β between the *a* and *c* axes is $\beta = 102.308°$ (Ref. 1).

[18] Y. Oka and T. Kushida, J. Lumin. **18/19**, 678 (1979).

[19] R. C. C. Leite and S. P. S. Porto, Phys. Rev. Lett. **17**, 10 (1966).

[20] R. C. C. Leite and J. F. Scott, Phys. Rev. Lett. **22**, 130 (1969).

[21] Our recent measurements with higher spectral resolution show that the one-LO line with $\hbar\omega_{LO} = 32.2$ meV takes the maximum intensity at the energy a little lower than E_T. By correcting the experimental data for the absorption and reflection losses, it is found that the peak of the scattering intensity is located just at the resonance energy E_T, details of which will be reported elsewhere.

[22] S. Permogorov and V. Travnikov, Phys. Status Solidi B **78**, 389 (1976).

[23] J. J. Hopfield and D. G. Thomas, Phys. Rev. **132**, 563 (1963).

[24] T. Hayashi and M. Watanabe, Solid State Commun. **69**, 959 (1989).

[25] K. Cho and M. Kawata, J. Phys. Soc. Jpn. **54**, 4431 (1985).

[26] S. Rudin, T. L. Reinecke, and B. Segall, Phys. Rev. B **42**, 11 218 (1990).