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Two-photon resonant hyper-Raman scattering by optic phonons due to the 2*P* exciton of ZnSe

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We have studied experimentally, by using a titanium sapphire laser, two-photon resonant effect of hyper-Raman scattering by optic phonons in 90° scattering geometry for a ZnSe crystal. We have found a striking enhancement of the signal in resonance with the 2*P* excitonic state. From comparison of the result with the relevant two-photon absorption data, the present phenomenon can be interpreted in terms of the time-dependent perturbation formalism.

It is well established that hyper-Raman or two-photon excitation Raman spectroscopy provides a useful tool, complementary to Raman spectroscopy, for studying phonon[1] or molecular vibrations.[2] In addition to being accessible to Raman-forbidden phonons, hyper-Raman spectroscopy has the advantage that a photon energy half that for Raman spectroscopy suffices for exciting the signal. This advantage may be useful in resonant light scattering spectroscopy, which we are concerned with, in particular in the ultraviolet region. Recently, resonant effects, in particular, a two-photon resonant effect of phonon hyper-Raman scattering has attracted increasing attention,[2,3] but as far as solid-state materials[4-6] are concerned, the study is still in an early stage. That is, fundamental aspects such as the symmetry of the electronic states causing resonant enhancement have not been clarified yet. This situation contrasts with that for resonant Raman scattering,[7] which has been extensively studied and consequently has served as one of the powerful methods for studying band structure as well as a particular electronic state.

In order to gain information about the character of the electronic state giving rise to the two-photon resonance of phonon hyper-Raman scattering in solids, we have experimentally studied the resonant behavior for a simple case, i.e., for 1*S* and 2*P* exciton states possessing different symmetries or parities with each other. For this purpose, a ZnSe crystal was used, since for ZnSe, with cubic symmetry ($\bar{4}3m$), Wannier-type excitons with a simple structure are known to exist. In this paper, we report experimental observation of a salient resonant feature of the LO-phonon signal in resonance with the 2*P* exciton, rather than the 1*S* exciton.

A thin-film ZnSe sample 5 μm thick was used. The good-quality sample was epitaxially grown on a GaAs substrate with the z axis normal to the film. The sample was directly immersed into liquid helium with a conventional cryostat. For excitation, a homemade titanium sapphire laser, with the output laser wavelength tunable over a wide near-infrared region, was employed. The laser, pumped by second-harmonic light from a *Q*-switched Nd:YAG laser (Quantronix, model 532) (YAG is yttrium aluminum garnet), had the representative characteristics of 1-kW peak power, 40-ns pulse width, and 3-cm^{-1} spectral width, and was operated at a 3-kHz repetition rate. The experiment was performed in the 90° scattering geometry, i.e., in $x(yy, x \text{ or } y)z$ or $x(zz, x \text{ or } y)z$, where the first two and the second symbols in the parentheses refer to the polarizations of incident and scattered lights, respectively. Note that two normal modes[8] of TO and LO phonons exisiting at the Brillouin zone center are both allowed[9] in $x(yy, x)z$ or $x(zz, x)z$ geometry but second-harmonic generation (SHG) in any direction is forbidden[10] for these incident polarizations. The laser beam was focused by a 5-cm focal-length lens on the sample along the x axis in the layer. The scattered radiation emitted normal to the layer (z axis) was collected by a lens on the entrance slit of a monochromator (Ritsu Co., MC-25N) of 29-Å/mm inverse dispersion, and detected by a cooled ($-35\,^\circ$C) optical multichannel detector[6] (Tracor-Northern, TN-6133).

In Fig. 1, examples of the scattering spectrum are shown, observed by using an excitation photon for which twice the incident photon energy $2\hbar\omega_i$ almost coincided with the 2*P* excitonic transition energy. A hyper-Raman signal is clearly discernible with the LO-phonon energy[8] of 251 cm^{-1}. Note that the absolute energy of the spectral line shifts with excitation photon energy, indicating

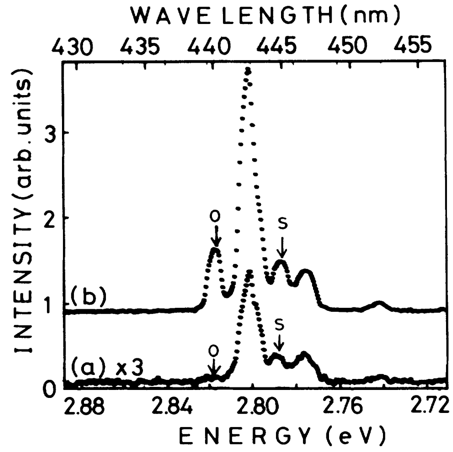

FIG. 1. Examples of the resonant hyper-Raman spectrum of ZnSe observed in the $x(zz, \text{unspecified})z$ geometry. The spectra were excited by using incident photon with the wavelengths (a) 8798 A and (b) 8804 A. Note that the signal denoted by *S* shifts with incident photon energy (the arrow with *O* indicates the position of $2\hbar\omega_i$). A large signal around 4425 A is a recombination emission (luminescence) from the 1*S* exciton.

that its origin is undoubtedly scattering, rather than emission. A weak SHG signal forbidden by the usual selection rules was observed at $2\hbar\omega_i$ (denoted by arrow "O") due to a higher-order process. A few emission lines with fixed absolute energies were also observed, which can be assigned to luminescence from the free and bound $1S$ excitons to which the $2P$ excitons decay through relaxation processes.

In a similar way, we have observed the spectra with incident photon energy varied to sweep through the exciton region. A plot of the intensity of the hyper-Raman signal as a function of $2\hbar\omega_i$ (two-photon excitation spectrum) is shown in Fig. 2, where the $x(zz$, unspecified$)\, z$ geometry is adopted. There, the energy positions of the $1S$ and $2P$ excitonic transitions are also marked for comparison, where the lower (higher) position corresponds to the exciton associated with the light (heavy) hole. Those positions were determined from one- and two-photon excitation spectra for the luminescences from the bound or free $1S$ exciton. It is remarked that the data points around the $1S$ exciton are obtained by smearing out the existing complicated fine structures, caused presumably by the polariton effect[11] as well as strain, which will be described later. This is because we are concerned with the scattering efficiency rather than the fine structure there. It is clearly seen in Fig. 2 that a striking enhancement of the signal occurs just in resonance with the $2P$ excitonic transition, and furthermore a weaker enhancement also manifests itself in resonance with the $1S$ exciton. The enhancement factor for the former amounts to almost 10^3 as compared to the off-resonant case just below the $1S$ exciton.

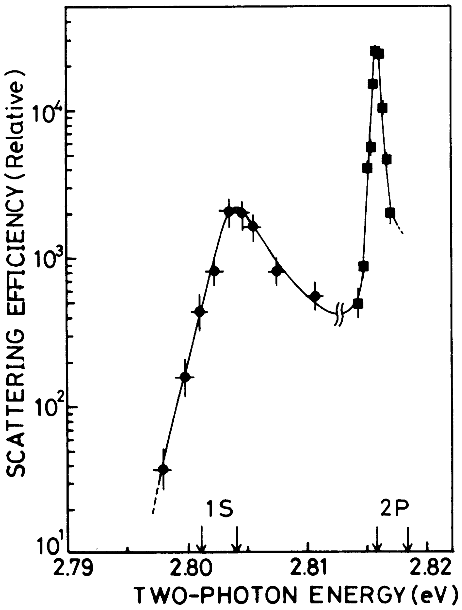

FIG. 2. Excitation spectrum of hyper-Raman scattering by LO phonon in the exciton region of ZnSe, which was observed in the $x(zz$, unspecified$)z$ geometry. The data points (●) below 2.81 eV represent the average ones over three runs. The positions of the $1S$ and $2P$ excitons are marked by arrows. The line is a guide to the eyes.

To clarify the origin of this resonance, we have also examined in detail the polarization dependence of incident light only around the $2P$ excitonic transitions. The result is shown in Fig. 3(a). It should be worth comparing the result with the relevant two-photon absorption spectra, which are shown in Fig. 3(b), more exactly, two-photon excitation spectra[12] for the luminescence signal from the $1S$ free exciton. The reason why only the $2P$ exciton region was examined in detail is that any luminescence signal did not appear for two-photon absorption around the $1S$ region. In Fig. 3(b), two peaks emerge with different polarization dependence. The splitting of the $2P$ exciton states, which are composed of the highest valence band of $J=\frac{3}{2}$ and the lowest conduction band of $J=\frac{1}{2}$, can be well interpreted[12] as arising due to residual internal strains of the present layer. Namely, slight in-plane biaxial strains arising from lattice misfit between ZnSe and the GaAs substrate give rise to splitting of the fourfold spin-degenerate valence band of $J=\frac{3}{2}$ into two bands of $J_z=\pm\frac{3}{2}$ and $J_z=\pm\frac{1}{2}$, causing two separate $2P$ exciton states. The polarization dependence provides unambiguous evidence for the interpretation. It can be shown[12] that the polarization dependence reflects the symmetry character of the $1S$ exciton, which is known to be the dominant intermediate state in two-photon absorption. Now the two spectra in Figs. 3(a) and 3(b) determined experimentally

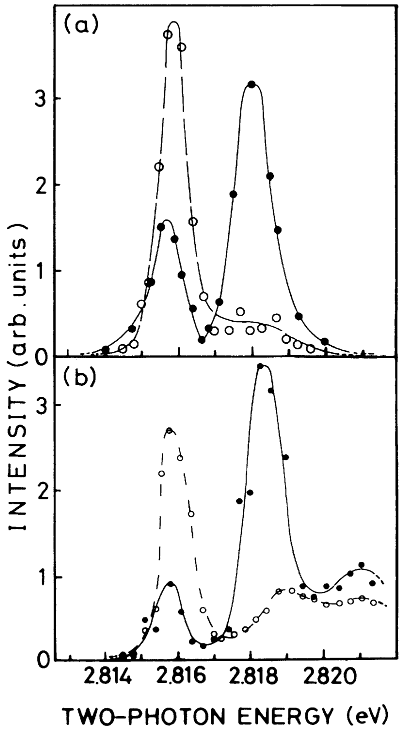

FIG. 3. A comparison between (a) excitation spectrum of hyper-Raman scattering by LO phonons and (b) two-photon absorption spectrum in the $2P$ exciton region of a 5-μm-thick ZnSe film. The dependence on the polarization of incident light was examined in detail for both spectra: ● and ○ correspond to the $x(yy$, unspecified$)z$ and $x(zz$, unspecified$)z$ geometries, respectively. The lines are a guide to the eyes.

are shown to be very similar to each other.

This allows us to understand microscopically the mechanism of the $2P$ exciton resonance. Relying on time-dependent perturbation calculation,[13,14] the major contribution to the relevant hyper-Raman process or tensor may come from such a term as

$$\sum_{l} \frac{p_{g,1S} H^{e\text{-LO}}_{1S,2p} p_{2p,l} p_{l,g}}{(E^{1S}-2\hbar\omega_i+\hbar\omega_{\mathrm{LO}})(E^{2p}-2\hbar\omega_i+i\Gamma_{2p})(E^{l}-\hbar\omega_i)},$$

where $\hbar\omega_{\mathrm{LO}}$ and Γ_{2p} represent the LO-phonon energy and the damping constant, respectively; l denotes either the $1S$, nS ($n=2,3,\ldots$) excitons, or the conduction band which is allowed through dipole transition, and $H^{e\text{-LO}}$ the interaction Hamiltonian between an electron and a LO phonon. Since the two-photon absorption spectrum for the $2P$ exciton is also governed by a similar term such as

$$A\left|\sum_{l} p_{2p,l} p_{l,g}(E^{l}-\hbar\omega_i)^{-1}\right|^2 \operatorname{Im}(E^{2p}-2\hbar\omega_i+i\Gamma_{2p})^{-1},$$

it may be quite reasonable to have the similar results shown in Figs. 3(a) and 3(b). Note that the first denominator remains almost constant when $2\hbar\omega_i$ is varied around the $2P$ exciton region. Nevertheless, the denominator $(E^{1s}-2\hbar\omega_i+\hbar\omega_{\mathrm{LO}})$ contributes considerably to the enhancement, since the term becomes as small as 16.5 meV if the value of 15 meV for $(E^{2p}-E^{1s})$ is used. In other words, the present phenomenon concerning the $2P$ exciton has a doubly resonant character, which presumably provides a reasonable explanation of the fact that the normalized scattering efficiency[15] proportional to the square of the hyper-Raman tensor, is anomalously large, say, at least 4 orders of magnitude larger for the present resonant signal as compared to the typical value for other materials observed in off-resonance experiments.

Next, the observed widths of 1.2 meV for the excitation spectra in Fig. 3(a) may be thought of as arising mainly from inhomogeneous broadening due to the fine structures. Microscopically, it is established[16] that the effect of a P-like envelope ($L=1$) and a hole ($J=\frac{3}{2}$) coupling yields a splitting of the degenerate $2P$ exciton state into three fine-structure components of $P_{1/2}$, $P_{3/2}$, and $P_{5/2}$. The present resolution of 0.4 meV was obviously not sufficient to observe the fine structure. More importantly, if the above envelope-hole coupling states are taken into account as intermediates, it follows from symmetry considerations that both x- and y-polarized signals should be observed, in contrast to the off-resonance case where only the x-polarized signal is seen, as already described. Experimentally, it is confirmed that this is indeed the case.

As for the resonance peak around the $1S$ exciton shown in Fig. 2, information on two-photon absorption, which should be a clue to understanding the mechanism, is lacking and so it is not clear to us at present. However, we would like to speculate briefly on the mechanism below. We point out first that the inability to observe two-photon absorption for the $1S$ exciton may be reasonable, because this is a general trend[17,18] for the $1S$ Wannier exciton in II-VI and III-V compounds. Despite this fact, the present experiment has revealed that rather strong resonance occurs even in the $1S$ exciton region. The most likely process to cause this resonance will be that involving successive virtual transitions described by $P_{g,1s} H^{F}_{1s,1s} P_{1s,2p} P_{2p,g}$, where $H^{F}_{1s,1s}$ is the q-dependent Fröhlich interaction.[7] However, a theoretical estimation based on the polariton picture, of the scattering efficiency for the process involving the $1S$ exciton will be made in a forthcoming paper after detailed experimental information has been obtained, including resonance Raman scattering as well as the polariton feature around the $1S$ exciton in the present sample.

Finally, we briefly discuss a spectroscopic use of resonant hyper-Raman scattering. We have provided a firm basis for exploring, by hyper-Raman scattering, electronic states with different parity from those allowed in resonant Raman spectroscopy. This method is basically similar to direct two-photon absorption spectroscopy, which may be rather difficult for thin samples such as superlattices. Two-photon absorption spectroscopy utilizing emission as a probe, which might be easy only if the luminescence signal is intense, does not reflect correctly the relevant density of states. Hence, resonant hyper-Raman spectroscopy is attractive. The present spectroscopy has also the advantage that it may be capable of exploring both $1S$ and $2P$ excitonic transitions simultaneously, and that incident photon energy of half the transition energy is sufficient. This is valuable in the ultraviolet region where a useful laser is not readily available, even if a particular transition can be allowed in resonant Raman scattering.

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