

Resonant Raman scattering at exciton intermediate states in ZnO

M. R. Wagner*, P. Zimmer, A. Hoffmann, and C. Thomsen

Technische Universität Berlin, Institut für Festkörperphysik, Hardenbergstr. 36, 10623 Berlin, Germany

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* Corresponding author: e-mail markus.wagner@physik.tu-berlin.de, Phone +49-30-31424440, Fax +49-30-31422064

We present results on resonant Raman scattering in single crystal ZnO using a continuously tuneable excitation in the energy region of the free and bound excitons. The PL and Raman spectra show the presence of a dominant luminescence band at 3.310 eV as well as the $A_1(\text{TO})$, $E_2(\text{high})$, $E_1(\text{LO})$, and $2E_1(\text{LO})$ Raman modes at liquid nitrogen temperature. A strong resonance of the Raman scattering cross

section was found for the second-order $2E_1(\text{LO})$ phonon mode. This enhancement is considerably larger than for the non-polar $E_2(\text{high})$ mode due to Fröhlich interaction. Furthermore, the resonance enhancement at bound excitons was studied at liquid helium temperature proving the essential role of excitonic intermediate states for resonant Raman scattering in ZnO.

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ZnO is a highly promising material for a wide variety of next-generation applications. As a wide-bandgap semiconductor with an energy gap of 3.37 eV at 300 K and a large free exciton binding energy of 60 meV [1], ZnO is an ideal candidate for optoelectronic devices such as blue to UV light emitting diodes or lasers and transparent electronics. The performance of optoelectronic devices is greatly affected by the vibrational properties of the material, which are influenced by the interaction of phonons with free and bound electron hole pairs. A powerful method to elucidate these processes is Raman scattering with excitation energies in the vicinity of excitonic states.

Resonant Raman scattering (RRS) in ZnO was first reported by Scott in 1970 [2], followed by more extensive studies by Oka et al. [4] and Calleja and Cardona [5]. Recently, the renewed interest in ZnO led to additional publications including RRS in ZnO thin films and nanostructures [6–8]. However, most of the reported experiments were conducted using the 325 nm line of a HeCd laser or the 351 nm and 364 nm lines of an Ar⁺ laser for excitation, while the resonance condition was achieved via the Varshni shift of the bandgap by varying the temperature. This method brings about certain difficulties such as the dissociation of bound excitons and the incomparability of intensities due to temperature dependence, which compli-

cate or even preclude a comprehensive study of the exciton–phonon interaction in resonance with excitonic states.

In order to investigate the resonance enhancement of Raman scattering at excitonic states, we applied a continuously tunable frequency-doubled titan–sapphire laser in the wavelength regime between 350 nm and 400 nm. The measurements were performed at different temperatures, thus enabling the study of resonance enhancements at free and bound excitons for arbitrary excitation energies in the resonance region. All presented spectra were acquired in backscattering geometry with the incident light oriented perpendicular to the crystal *c*-axis. The ZnO single crystal was mounted in a bath cryostat operating at suprafluid helium temperature (1.8 K) or liquid nitrogen temperature (77 K).

The photoluminescence spectra at 77 K for different excitation energies between 3.256 eV and 3.357 eV are depicted in Fig. 1. The narrow line at the high energy side of each spectrum represents the specific laser excitation. For high excitation energies, a dominant luminescence at 3.310 eV with two phonon replicas can be observed. Although frequently observed, the origin of this luminescence remains controversial. Possible explanations are deeply bound excitons at structural defects, band-acceptor transitions (e, A), or donor-band transitions (D, h). How-

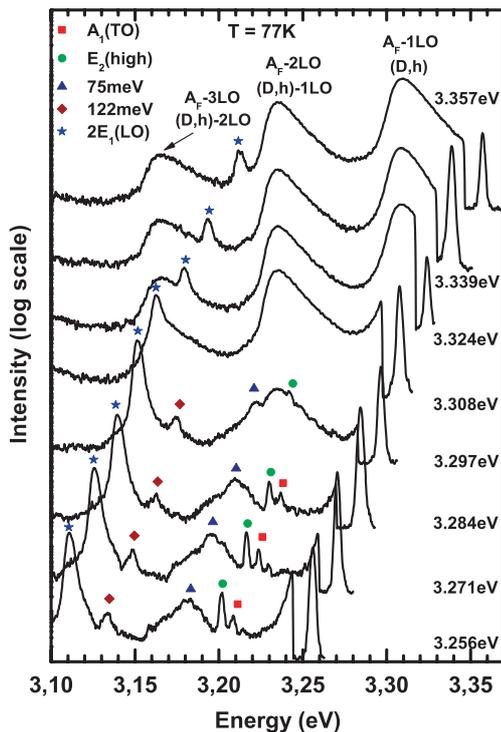


Figure 1 (online colour at: www.pss-rapid.com) Spectra for various excitation energies at 77 K. The $2E_1(\text{LO})$ Raman mode is present in all spectra, the other luminescence and Raman lines can be observed in dependence on the laser energy.

ever, the asymmetric shape and large half-width of the luminescence band are not consistent with the usually narrow and thermally less stable exciton luminescence at structural defects. Also, the absence of a donor–acceptor pair (DAP) at low temperatures (Fig. 4) renders the attribution to a (e, A) transition unlikely. Consequently, we attribute the luminescence band at 3.310 eV to a (D, h) transition. This luminescence band is superimposed by the 1LO phonon replica of the free exciton A_F for large excitation energies. This assignment is also supported by the presence of a short excitonic and a long defect related time constant with an amplitude ratio of approximately 10 to 1, underlining the dominance of the phonon replica of the free exciton.

In addition, we observe a phonon mode in the first spectrum at 3.212 eV, which shifts with the excitation energy at a constant distance of 144.8 meV (1168 cm^{-1}) from the laser. This energy equals twice the energy of the $E_1(\text{LO})$ Raman mode (584 cm^{-1}) [5], evidently identifying this line as a second order $2E_1(\text{LO})$ Raman mode [4]. For an excitation energy of 3.308 eV, the energy of the $2E_1(\text{LO})$ Raman line matches that of the phonon replica at 3.165 eV leading to a superposition of the luminescence and Raman signals in the spectra. As the laser is tuned to lower energies, the appearance of additional Raman modes can be noted which are not visible at higher excitation energies due to the strong luminescence background. However, for lower excitation energies, the (D, h) luminescence

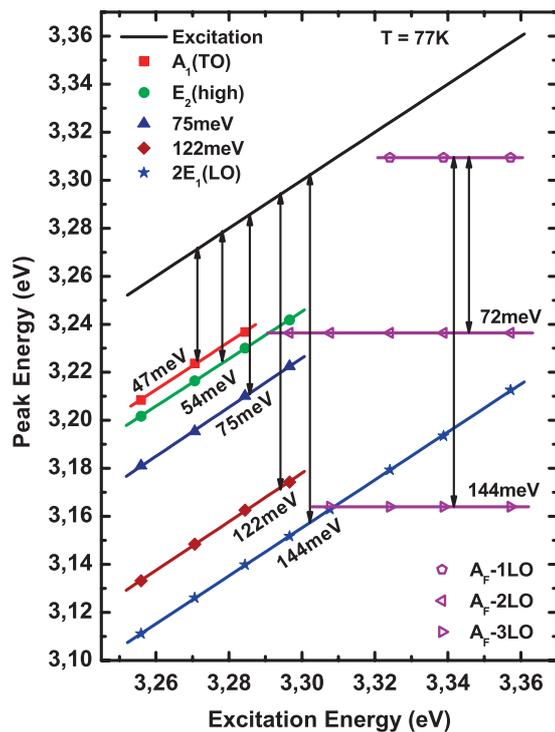


Figure 2 (online colour at: www.pss-rapid.com) Peak energy as a function of the excitation energy at 77 K. Raman lines shift linearly with the excitation energy, while the free exciton luminescence and phonon replicas remain at constant photon energies.

cannot be excited, consequently leading to the disappearance of the phonon replicas. We identify the lines at a distance of 47.2 meV (381 cm^{-1}) and 54.2 meV (437 cm^{-1}) from the laser line as the transverse optical $A_1(\text{TO})$ mode and the non-polar optical $E_2(\text{high})$ mode, respectively. As expected, the $E_1(\text{LO})$ mode is not visible in backscattering geometry. Instead, we observe a rather broad peak with the maximum at a distance of 75 meV (605 cm^{-1}) possibly resulting from higher order scattering involving TA phonons. Furthermore, a Raman line at 122 meV (984 cm^{-1}) can be observed. That mode has first been described by Damen et al. as a multiphonon process [3]. A recent publication attributes this line to an $A_1(2\text{TO})$ process involving phonon wave vectors considerably displaced from the zone center [8].

The energies of the observed Raman as well as luminescence peaks as a function of the excitation energy are illustrated in Fig. 2. The horizontal lines represent the luminescence peaks at a constant energy, which appear for excitation energies higher than or equal to the energy of the dominant luminescence, while the inclined lines show the shifting of the Raman modes with constant distance to the laser excitation. Except for the strong $2E_1(\text{LO})$, these lines are only visible for excitation energies lower than that of the defect band at 3.310 eV. The clear presence of the $2E_1(\text{LO})$ mode, even at larger laser energies, prove that the scattering mechanism of the $2E_1(\text{LO})$ mode is strongly enhanced near the resonance region.

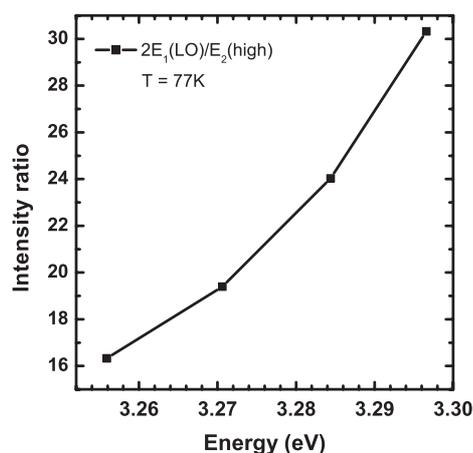


Figure 3 Intensity of the $2E_1(\text{LO})$ mode normalized to the intensity of the $E_2(\text{high})$ phonon mode as a function of the excitation energy at 77 K. Lines are a guide to the eye only.

Evidently, the $2E_1(\text{LO})$ peak dominates the Raman spectrum for lower excitation energies and exhibits a significant rise of intensity compared to the $E_2(\text{high})$ mode for increasing excitation energy toward the free exciton energy (Fig. 3). The non-polar $E_2(\text{high})$ mode interacts only via the deformation potential, while the polar LO modes are also subject to Fröhlich interaction. Hence, the increased intensity ratio towards the free exciton resonance energy due to the Fröhlich interaction implies the scattering mechanism to be mediated via a real excitonic state.

The resonance enhancement of the Raman scattering at bound excitons was studied at 1.8 K. The excitonic luminescence for above bandedge excitation shows several sharp lines associated with bound exciton recombinations between I_0 and I_{10} , which are dominated by the most intense I_9 line at 3.357 eV. Figure 4 displays the spectra for three different excitation energies (above bandedge, in resonance with the free exciton A_F and in resonance with the bound exciton I_9). The intensity of the A_F -1LO line was normalized in all spectra for comparability reasons. Apparently, the $2E_1(\text{LO})$ mode in the first spectrum is very weak, indicating a small Raman cross section. The first and second phonon replicas of the bound exciton transition were found to be of similar intensity. For resonant excitation at the free exciton (3.377 eV), we observe an increase in the $2E_1(\text{LO})$ Raman intensity. This enhancement culminates in a strongly increased 2LO intensity as the incident photon energy is in resonance with the dominant bound exciton I_9 at 3.357 eV. This provides direct evidence that the increased 2LO Raman cross section is contingent on the excitation of bound exciton states.

In summary, we presented experimental evidence for resonant Raman scattering in ZnO. The intensity of the polar $2E_1(\text{LO})$ mode shows the strongest enhancement. This

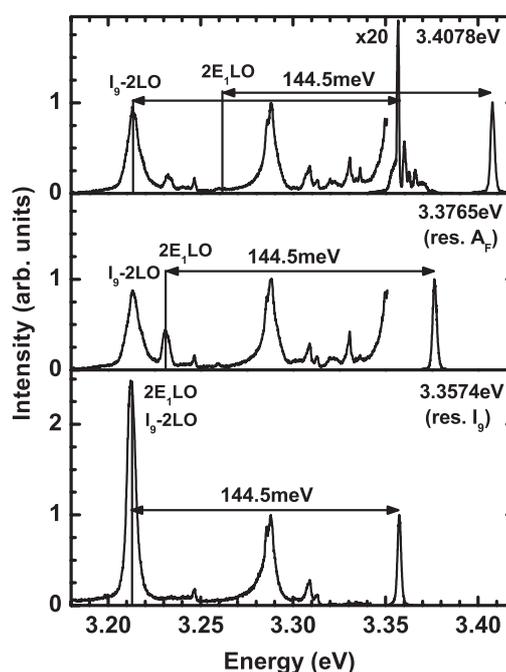


Figure 4 Low temperature spectra (1.8 K) of resonant Raman scattering at bound excitons. From top to bottom: excitation above band edge, in resonance with the free exciton A_F , and in resonance with the bound exciton complex I_9 .

is attributed to a large Fröhlich interaction which is reflected by the $2\text{LO}/E_2(\text{high})$ intensity ratio since the $E_2(\text{high})$ is only subject to electron–phonon interaction via the deformation potential. The experimental results emphasize the impact of exciton intermediate states on an enhanced cross section for resonant Raman scattering.

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