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Terahertz modulation of the blue photoluminescence in ZnSe

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We report on effective optical modulation of blue PL in ZnSe with a powerful pulse from a free-electron laser operating in the THz range. A 30% resonant quenching is observed for a quantum energy $E_{FEL} \approx 107$ meV. This resonant feature is replicated at higher photon energies, with several equidistant maxima separated by 33 meV. We identify the PL emission quenching with ionization of shallow acceptor states participating in the donor-acceptor pair recombination responsible for the blue emission. The possiblility of Fano-resonances ooccuring in this system are discussed. Such resonances can appear due to strong coupling between shallow acceptor states and longitudinal phonons.

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I. INTRODUCTION

The wide gap semiconductor ZnSe receives considerable attention as a suitable material for blue-green laser diodes, mid-infrared lasers, and other optoelectronic devices. This interest has recently been renewed and strengthened by prospects of applications in spintronics[1,2] as well as for energy upconversion and THz generation in a two-step optical pumping regime.[3] For all these purposes, the availability of high-quality crystals with tailored electrical parameters as well as a detailed understanding of electronic structure and properties are necessary prerequisites. However, the production of high-quality ZnSe crystals represents still an unresolved challenge. Among others, the possible origin of the difficulties might be related to a strong electron-phonon coupling. In ZnSe, the relatively large effective masses of carriers and the large difference between the values of static and high-frequency dielectric constants increase the polarization interaction with optical phonons. This gives rise to interesting physical phenomena that could be also of practical relevance.

The application of a free-electron laser (FEL) for two-color spectroscopy in the visible and the mid-infrared, is a very powerful and versatile experimental approach to investigate energy flows in optically active semiconductors.[4] In the past, this method has been successfully applied for the identification of excitation mechanisms in rare-earth-doped matrices[5–8] and phonon-related excited states of atomic clusters.[9,10] In that case a pump laser, operating in the visible, provides band-to-band excitation of the host material resulting in the generation of free carriers and in the transient population of shallow traps. Carriers localized at these levels are then released to the band upon the application of the free-electron probe laser of which the energy quantum can be tuned to the trap ionization energy. At the same time, illumination with photons of mid-infrared energy quantum can lead to the generation of phonons (lattice and/or local).

II. SETUP AND SAMPLE

In the reported study, we have applied free-electron laser two-color mid-infrared (2C-MIR) spectroscopy to investigate the blue anti-Stokes luminescence band (around 2.7 eV) in Cr-doped ZnSe and, in particular, the shallow centers responsible for this emission. In addition to 2C-MIR experiments, also photoluminescence (PL), and photoluminescence excitation (PLE) spectroscopies have been used. The 2.7 eV blue emission is identified as being due to donor-acceptor pair (DAP) recombination.[11,12] We have observed a very effective (up to approximately 30%) reduction in PL intensity $\Delta I/I$ (hereafter called quenching) of the DAP emission upon the application of a powerful mid-infrared pulse. The magnitude of the quenching effect has a pronounced dependence on FEL quantum energy, including several equidistant maxima, with the first one at $E_{\mathrm{FEL}} \approx 107$ meV. The separation between these maxima is equal to the value of an optical phonon of ZnSe. We identify the observed PL quenching effect as being due to the ionization of shallow acceptors participating in the DAP recombination, and several phonon replica. The possibility that the FEL-induced quenching of PL is modulated by Fano resonances[13] is discussed in detail.

The current study has been performed on Cr-doped ZnSe crystals grown from melt by the Bridgman-Stockbarger technique and purified by a subsequent treatment in the Zn melt. The Cr doping level was $[\mathrm{Cr}]=4.2\times10^{18}$ cm^{-3}. Besides Cr, the SIMS analysis also revealed the presence of Al, Cl, and Li impurities, with concentrations of 5×10^{17}, $<10^{17}$, and $\sim3\times10^{17}$ cm^{-3}, respectively. Previous studies have shown that Cr doping enables an efficient energy upconversion in ZnSe via a two-step photon absorption process.[14] Therefore blue DAP-related emission can be induced in ZnSe:Cr with photons of subband energy quantum. In this case, the volume of a sample can be effectively pumped. Figure 1 illustrates the experimental setup for 2C-MIR measurements, as used in the reported project. These were performed at the FELIX-

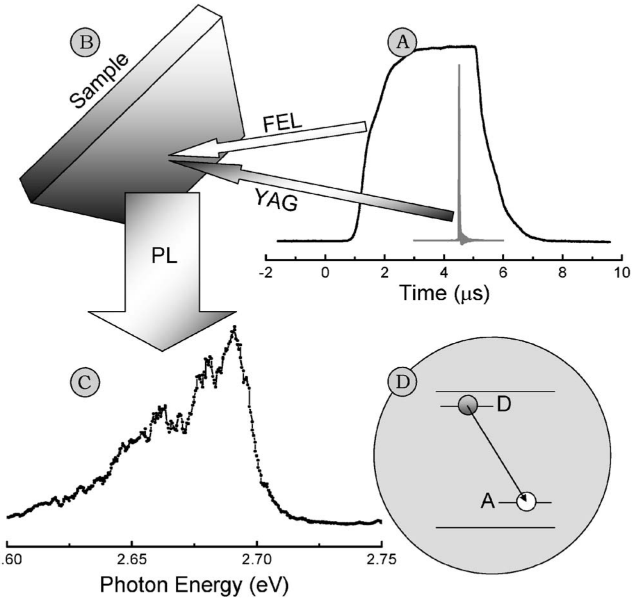

FIG. 1. Schematics of the two-color mid-infrared spectroscopy setup with a free-electron laser used in the experiment. The ZnSe:Cr sample (B) is excited with pulses from both a Nd:YAG laser (second harmonic) and a FEL (A). The resulting PL spectrum (C) is recorded. The PL shown is due to donor-acceptor pair recombination (D).

users facility (free-electron laser for infrared experiments) in Nieuwegein, the Netherlands. The sample is placed in a helium gas flow cryostat and excited directly with the second harmonic of a Nd:YAG pulsed laser (A and B), at a (subband) wavelength of 532 nm. On the detection side, the spectrometer is tuned to the blue DAP band (C and D). During the experiment, we follow the change of intensity of this emission, as induced by a pulse from the FEL. This pulse is applied in such a way that it overlaps in time with the excitation provided by the Nd:YAG (for details of the 2C-MIR spectroscopy with FEL see, e.g., Ref. 5).

III. EXPERIMENTAL RESULTS

Figure 2 summarizes the major experimental finding of this study. In the figure the intensity change of the blue DAP emission, detected at $E_{\mathrm{DAP}}=2.68$ eV and normalized to the level unmodulated by the FEL, is plotted as a function of the FEL photon energy. A very strong PL quenching is observed; it is characterized by several equidistant maxima superimposed on a broader background. The first maximum is found for $E_{\mathrm{FEL}} \approx 107$ meV and amounts to $\sim 30\%$ of the original PL intensity. This resonant feature is replicated at higher FEL photon energies, with an energy separation of ~ 33 meV.

Photoluminescence of the ZnSe:Cr sample used for the 2C-MIR experiments is shown in Fig. 3, where low-temperature spectra obtained by excitation at various excitation photon energies in the range from 2.722 to 2.829 meV are given. For these measurements, the sample was placed in an optical closed-cycle cryostat and cooled to a temperature of 10 K. An optical parametric oscillator system pumped with the third harmonic of a Nd:YAG laser and covering a

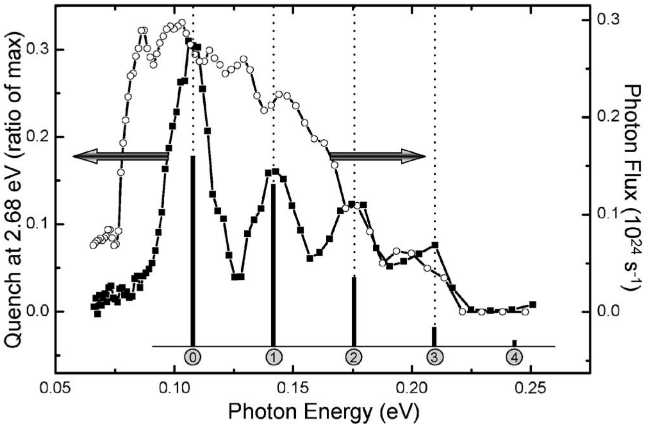

FIG. 2. Quenching of the 2.68 eV DAP photoluminescence as a function of the FEL photon energy. The quench is normalized with respect to the full signal (unquenched). Oscillations of the quenching effect are clearly visible with an energy separation of about 33 meV. This value is similar to the energy of phonons observed in PL of band excitonic recombination (Fig. 3). The measured flux density in the FEL pulse is also given (right scale).

0.56–3.1 eV variable photon energy range was used for excitation. The emerging PL was dispersed with a grating spectrometer and detected using a photomultiplier tube. As can be seen in Fig. 3, around 2.7 eV, a strong asymmetric emission band due to donor-acceptor recombination appears. Similar DAP spectra have been observed before for DAP recombination in heavily Cr-doped ZnSe crystals, with the additional structure of the main peak being due to the available acceptor states. A somewhat more careful inspection reveals that the asymmetry is due to phonon replicas that appear on the low-energy side of the band. Phonon-related

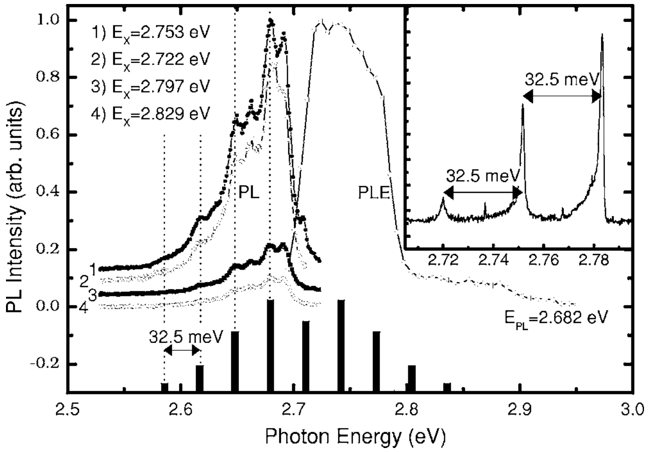

FIG. 3. PL and PLE spectra of ZnSe:Cr. To the left, four spectra, taken at various excitation photon energies, are given. As can be seen, the characteristic spectral features do not change within the investigated excitation energy range. The right curve is the PLE spectrum measured at a fixed PL energy of 2.682 eV. Three phonon replicas can be distinguished. The phonon energy is identical to that observed for the replicas of bound-exciton luminescence in a Cr-free ZnSe crystal (see the inset). The bars represent the calculated distribution of phonon replica's using $\zeta_0^2=2.5$ in Eqs. (3) and (4)—see the text for a further explanation.

replication is a well-known feature of PL bands in ZnSe. In the inset of Fig. 3, it is illustrated for bound-exciton recombination in a Cr-free ZnSe crystal; in this case, three sharp phonon replicas of the bound exciton recombination can be distinguished, with a phonon energy of $\hbar\omega = 32.5$ meV. The DAP origin of the 2.7 eV band observed in the current study for the ZnSe:Cr sample is consistent with thermal quenching of its intensity—not shown—from which an activation of $E_{\text{th}} \approx 30$ meV is derived. It is reasonable to assume that this energy corresponds to the ionization energy of donors in the sample.

Also the excitation spectrum (PLE) of the DAP band, as measured with the spectrometer set to 2.682 eV, is shown in Fig. 3. As can be seen, the PLE spectrum (direct excitation) is shifted with respect to the PL band toward higher photon energy.

IV. DISCUSSION

In order to rationalize our findings, we note that the carrier coupling with longitudinal optical phonons is strong in ZnSe due to the large difference in the values of high-frequency $\varkappa_\infty$ and static $\varkappa_0$ dielectric constants: $\varkappa_\infty = 6.25$ and $\varkappa_0 = 9.1$. The polaron shift induced by the polarization interaction with longitudinal optical phonons to the ground energy level of a shallow Coulomb center can be calculated by using the second-order perturbation theory (see, e.g., Ref. 15):

$$\Delta\epsilon_p = \sum_n \sum_{\vec{q}} \frac{2\pi e^2 \hbar\omega}{Vq^2 \varkappa^*} \bullet \frac{\langle\varphi_0|e^{i\vec{q}\cdot\vec{r}}|\varphi_n\rangle\langle\varphi_n|e^{-i\vec{q}\cdot\vec{r}}|\varphi_0\rangle}{(\hbar\omega + \epsilon_n - \epsilon_0)}. \qquad (1)$$

Here $\vec{q}$ and $\hbar\omega$ are the optical phonon wave vector and energy; V is the normalization volume; φ_0, ϵ_0 and φ_n, ϵ_n are the wave functions and energies of the ground and the excited Coulomb states, correspondingly, and

$$\frac{1}{\varkappa^*} = \frac{1}{\varkappa_\infty} - \frac{1}{\varkappa_0}. \qquad (2)$$

If we take into account only the main (first) $n=0$ term in the sum over n in Eq. (1), we get, after a simple calculation,

$$\Delta\epsilon_p = \frac{5e^2}{16\varkappa^* \hbar}\sqrt{2\epsilon_0 m}, \qquad (3)$$

where ϵ_0 and m are the binding energy and effective mass of a bound carrier in the ground Coulomb state, respectively.

Electron and hole effective masses in ZnSe are equal to $m_e = 0.21 m_0$ and $m_h = 0.6 m_0$, correspondingly, m_0 being the mass of a free electron. This results in Bohr energies for donors $\epsilon_D = 39$ meV and for acceptors $\epsilon_A = 111$ meV. Thus, we have from Eq. (3) that the polaron shift due to the interaction with optical phonons is for donors $\Delta\epsilon_p^D \approx 10$ meV and $\Delta\epsilon_p^A \approx 30$ meV for acceptors. It should be noted that the strong electron interaction of carriers with longitudinal optical phonons in ZnSe, as well as polaron effects, were discussed in the literature in the past—see, e.g., Ref. 16. The sample under study contains Li acceptors and Al and Cl donors with concentrations in the $\sim 10^{17}$ cm^{-3} range. The relevant binding energies are 111 to 114 meV for Li acceptors, 25.6 to 26.3 meV for Al, and 26.1 to 26.9 meV for Cl donors.[17] Further, in view of this high concentration, some Li atoms could take interstitial lattice positions and act as donors.[18] Therefore, one can expect that the true polaron shifts for shallow impurities in the material under study might be somewhat smaller than the estimated value. In what follows, for simplicity, we shall discuss only the phonon coupling for holes, as it is considerably larger than for electrons. Moreover, since the concentration of donors in the investigated material exceeds that of acceptors, we could expect that the DAP recombination will be controlled by acceptors; this indeed is confirmed by the results of the study. For the analysis of experimental results, we only apply the simple one-mode (Huang-Rhys) model, as it is practically identical to a multimode model for multiphonon transitions with optical phonons with a small dispersion in energy.[15] Nevertheless, we note that phonon dispersion will contribute to the linewidth of absorption (and ionization) transitions.

We will consider optical transitions of a bound hole from the ground state into an excited state under MIR radiation. The relative probabilities of optical transitions assisted by emission of n phonons depend on the value of the polaron shift $\Delta\epsilon_p$. In the one-mode model, this is determined by the equilibrium shift of the configuration coordinate x_0:

$$\Delta\epsilon_p = \frac{M\omega^2}{2} x_0^2, \qquad (4)$$

where M is the impurity mass. The electron-phonon coupling should induce phonon replicas in the spectra of photoluminescence and excitation of a bound hole to a discrete level. If we introduce a dimensionless parameter $\zeta_0 = x_0\sqrt{M\omega/\hbar}$ for the polaron shift of the configuration coordinate, the energy of the polaron shift [Eq. (4)] can be presented in the form

$$\Delta\epsilon_p = \frac{\hbar\omega}{2}\zeta_0^2. \qquad (5)$$

From Eqs. (3) and (5) one can get the value of $\zeta_0^2 \simeq 1.7$ for acceptors in ZnSe. The hole transition probability $W_{0,n}$ assisted by emission of n phonons is determined by the overlap of oscillator wave functions of the ground and excited vibration levels and is given by[19]

$$W_{0,n} = \frac{w_e I_n}{\sum_{n=0}^{\infty} I_n}, \qquad (6)$$

and

$$I_n = \frac{\zeta_0^{2n}}{2^n n!}\exp\left(\frac{-\zeta_0^2}{2}\right), \qquad (7)$$

where w_e is determined only by the hole transition.

A comparison of PL and PLE spectra of DAP presented in Fig. 3 supports our estimation of the value of the polaron shift. The observed (though poorly resolved) phonon replicas in the DAP photoluminescence spectrum, the shift between the PL and PLE spectra, and the very wide range of the excitation spectrum (the same energy range as for PL) are results of strong electron-phonon coupling. The relevant peaks in the PLE spectrum could not be observed, but they are very often smoothened due to the dispersion of phonons, potential fluctuation, etc. A calculation using Eqs. (6) and (7) has been produced with parameter $\zeta_0^2=2.5$ because for DAP photoluminescence we should take into account the total polaron shift for donors and acceptors, which is about 40 meV. Good agreement with the experimental data is found.

Whenever the zeroth-order description of a system includes a discrete state degenerate with the continuum, Fano resonances[13] can occur for an optical transition at a single impurity involving an excited level. Any small interaction between the discrete state and continuum mixes them strongly in the neighborhood of the degeneracy, and thereby gives rise to an interference effect. Due to the strong hole-phonon coupling in ZnSe, as discussed above, such an effect can be expected also in this study. In this case, the continuum comprises hole states in the valence band and the localized state would be formed by a bound excited state of an acceptor together with one or several longitudinal optical phonons. Typically, a Fano resonance appearing in an absorption or photoconductivity spectrum exhibits a characteristic asymmetry, reflecting a decrease and increase of the transition probability in the vicinity of the degeneracy. Therefore the magnitude of this asymmetry, which is usually more pronounced in photoconductivity than in absorption spectra, depends on the magnitude of the coupling parameter between the band and the localized state. In the past, Fano resonances associated with emission of phonons were observed for shallow impurities in semiconductors both in absorption and in photoconductivity measurements.[20–24] In Ref. 24 a theoretical model was presented that offers an explanation for the difference between Fano resonances in absorption and photoconductivity spectra in case of weak electron-phonon coupling, which was experimentally found for dopants in silicon. The difference reflects the fact that there are different final-state channels for the initial excitation process, resulting in either a free carrier or a bound electron together with phonons that has left the center.

In the present study, we follow changes in the DAP-related PL. That implies that we monitor quenching of radiative recombination from the bound state, reflecting the decreasing population of this state. Due to a polaron shift of the ground state of the acceptor, as discussed, the hole transition to a sufficiently shallow excited state will be followed by ionization into the band, rather than a return to the ground state. Thus, the line shape of the relevant Fano resonance can be expected to resemble that observed in absorption.

Assuming the description above applies to our system, one is tempted to identify the MIR quenching spectrum depicted in Fig. 2 as arising from FEL-induced ionization of the acceptor participating in DAP recombination, modulated by Fano resonances related to emission of optical phonons. In order to test such a possibility, we present in Fig. 2 the distribution of phonon replicas calculated with $\zeta_0^2=1.7$. As can be seen, the observed peaks in the MIR-induced quenching of blue luminescence could be interpreted as Fano replicas, corresponding to resonant transition between the ground and an excited state of the acceptor followed by subsequent ionization into the band (0), and its replicas due to one- (1), two- (2), and three- (3) phonon-assisted Fano resonances. We note that the emission of phonons would have to take place simultaneously in one transition under the absorption of a photon during the (multi)phonon-assisted optical absorption process. In contrast to the earlier reports, where only one-phonon-assisted Fano resonances have been observed,[20,21,23,24] multiphonon replicas would be found in the present study, reflecting the aforementioned large carrier-phonon coupling characteristic for ZnSe. In order to confirm this, however, an accurate line shape analysis is neccessary, for which the quality of the measured MIR-induced quenching dependence is not sufficient.

Further continuing the interpretation of the PL quenching spectrum of Fig. 2, we assign the broad background underlying the resonant features as DAP recombination quenching, appearing due to direct ionization of holes from acceptors into the valence band, with an onset energy of ~110 to 120 meV, reflecting the ionization energy of the acceptor trap involved in the blue DAP recombination. In view of the sample characteristics, it is natural to identify the optically active state with a Li acceptor, of which the ionization energy has been determined as $E_{\mathrm{Li}}=111$ to 114 meV.[17] In that case, the prominent resonant feature (0) in the DAP quenching spectrum of Fig. 2 could be identified with the $1S_{3/2} \rightarrow 2P_{5/2}(\Gamma 8/\Gamma 7)$ resonant transition. The polaron-free energy of this transition has been estimated as 84.0/91.3 meV.[25]

V. CONCLUSION

Based on the current study, we conclude that intensity of the blue DAP luminescence in ZnSe can be modulated very effectively by THz radiation. In particular, we have demonstrated a strong 30% resonant quench upon illumination with MIR photons of energy $E_{\mathrm{FEL}} \approx 107$ meV, replicated at higher energies by simultaneous generation of lattice phonons. As the physical origin of this quenching effect, ionization of acceptor states is proposed, with resonant transitions of an acceptor-bound hole into a discrete excited state and its phonon-assisted replicas degenerate with the valence band. The possiblity of Fano resonances being observed in the quenching process as a modulation of the intensity of the DAP recombination band, has been considered. The presented report illustrates yet one more successful application of a free-electron laser-based technique for investigation of fundamental properties of matter.

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