Optical properties of excitons in GaTe

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We present photoluminescence and transmission measurements of vapor-grown GaTe crystals. The ground-state 1*S* triplet and singlet excitonic peaks are well resolved in the optical photoluminescence spectra from high-quality crystals, the triplet state lying ~ 1.6 meV lower in energy than the singlet state. The emission intensity ratio of these two peaks is close to the 3:1 ratio of their spin multiplicities. The 1*S* singlet-state emission is strongly polarized perpendicular to the crystal *b* axis, whereas the emission from the triplet state is partially polarized along the crystal *b* axis. Transmission spectra also indicate that the absorption corresponding to the $n=1$ exciton is made up of two peaks, of which the higher-energy one is observed only for light polarized perpendicular to the *b* axis. Two small peaks on the lower-energy side of the photoluminescence triplet peak are believed to correspond to 1*S* singlet and triplet excitons bound to a strain-induced defect center.

I. INTRODUCTION

III-VI layered semiconductor compounds such as GaSe and GaTe are of special interest, largely because some of their physical properties are highly anisotropic. They exhibit strong exciton spectra, and have potential applications for photon detectors and other optoelectronic devices.[1]

The GaTe structure is monoclinic with space group $C2/m$ (C_{2h}^3).[2-4] As shown in Fig. 1, each crystallographic unit cell proposed by Pearson[2] contains 12 molecules, analogous to SiAs and GeAs,[5] with the primitive cell containing six molecules. Because of the low symmetry and complex unit cells, each of which contains 108 valence electrons, no band-structure calculation is currently available. As in other layered semiconductors, intralayer forces are mainly covalent, with some ionic contribution, and interlayer forces are of weak Van der Waals type.

The layer structure of GaTe has been much less studied[6-11] than the other members of the layered III-VI family, such as GaSe, InSe, and GaS. The other III-VI compounds crystallize in a four-sheet [Se(S)-Ga(In)-Ga(In)-Se(S)] intralayer stacking pattern, with all of the Ga—Ga or In—In bonds lying perpendicular to the layer planes.[12] Two-thirds of the Ga—Ga bonds in GaTe are also (approximately) perpendicular to the layer planes; however a striking difference between GaTe and the others in the III-VI family is the orientation of the rest of the Ga—Ga bonds, which lie almost in the layer plane. These bonds are perpendicular to the twofold-rotational symmetry axis of the layers (*b* axis) and form chains that run *along* the *b* axis. Their presence introduces an abrupt change in optical and crystallographic properties when going from GaSe to GaTe.[11] The GaTe crystal layers extend along (102) planes (in the convention established by Pearson[2]) and have their growth direction along the *b* axis.

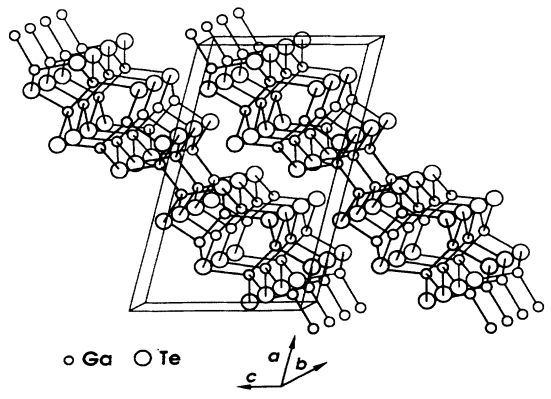

FIG. 1. Crystal structure of GaTe, as proposed by Pearson (Ref. 2).

There is no evidence of polytypism in monoclinic GaTe. A metastable phase of GaTe has been reported, consisting of GaSe-like Te-Ga-Ga-Te layers, ordered according to double-layer hexagonal stacking. Annealing for a short time at a temperature of ~ 100 °C resulted in conversion into the monoclinic structure.[13] In the layered semiconductors with the GaSe structure, stacking faults (grown-in, strain- or high-intensity laser-induced, etc.), which form easily, will normally reduce the symmetry of the mother crystals around the fault plane, and degenerate exciton states will be split by this small stacking-fault potential, giving fine structures of exciton states.[14] In monoclinic GaTe crystals, however, there is no rotational symmetry axis perpendicular to the layers and no low-energy alternative to the observed stacking pattern, so we expect that stacking-fault-related effects will not be observable.

In this paper, photoluminescence (PL) and transmission spectra of strong, narrow, well-defined band-edge excitons of vapor-phase-grown GaTe are presented.

II. EXPERIMENTS

We have synthesized single crystals of GaTe, using the iodine transport reaction technique. The layer structure of this compound gives rise to a specific growth habit, producing large but very thin flakes which are easily deformed and have mirrorlike surfaces. These platelets are especially convenient for optical measurements, since they require no cleavage or other mechanical treatment which can induce various defects. If the samples are handled very carefully, they are free from strain, and the intrinsic optical spectra can be well resolved. The typical size of a sample was $10\times4\times0.2$ mm^3.

GaTe single crystals, grown by iodine transport, closed-tube sublimation, and the Bridgman-Stockbarger method are all p type.[15] By analogy with GaSe and GaS,[16] the acceptor centers can be attributed tentatively to Ga vacancies, which are common in these types of compounds.

For temperatures below 40 K, low-excitation luminescence measurements were made using an Ar^+-ion laser (514.5 nm) as a continuous-wave excitation source. The maximum power density was ~20 W cm^{-2}, and by inserting calibrated neutral density filters into the laser beam the laser power density could be varied within wide limits. The beam was incident almost normal to the sample planes. The emission was collected from the excitation spot, dispersed by a 1-m ISA model U1000 double spectrometer, and detected by a cooled InGaAs photomultiplier tube using standard photon-counting techniques.

In order to study the polarization properties of emission lines, a polarizer was used to set the direction of the polarization vector **E** of the exciting light, and an analyzer was placed just in front of the entrance slit of the spectrometer.

For the transmission measurement, a quartz-halogen white-light source was focused onto the sample, which was oriented with the layer planes approximately perpendicular to the incident beam. A pinhole of diameter 2 mm was used to select a region of the sample that was free from twin boundaries and obvious defects. The sample was immersed in either superfluid liquid helium (for $T<2.2$ K) or helium vapor (for $T>4.2$ K). Transmitted light was analyzed using a Bomem DA3 Fourier-transform spectrometer with a quartz beamsplitter and a silicon photoconductive detector. Since this source-beamsplitter-detector combination gives a maximum intensity at wavelength $\lambda\sim1$ μm, we used an infrared absorbing filter to reduce the signal for $\lambda>0.7$ μm, which is just above the region of interest for this work. For polarization-dependent measurements, a polarizer was placed just before the sample, either parallel or perpendicular to the b axis. Reference spectra were taken under conditions identical to those for the sample spectra, with the sample removed from the beam.

III. RESULTS AND DISCUSSION

Figure 2 shows a typical PL spectrum from a fresh GaTe crystal. Two sharp peaks were found, at $X_1=1.7798$ eV, with full width at half maximum (FWHM) ~0.7 meV, and at $X_2=1.7782$ eV with FWHM ~0.5 meV, for temperature $T\sim8$ K, and laser excitation intensity $P\sim3$ W/cm^2. On the lower-energy side of peak X_2, two small peaks X_3 and X_4 appear at energies 1.7747 and 1.7732 eV (see inset), followed by a broad energy band ($1.76\rightarrow1.70$ eV) with maximum intensity at ~1.74 eV.

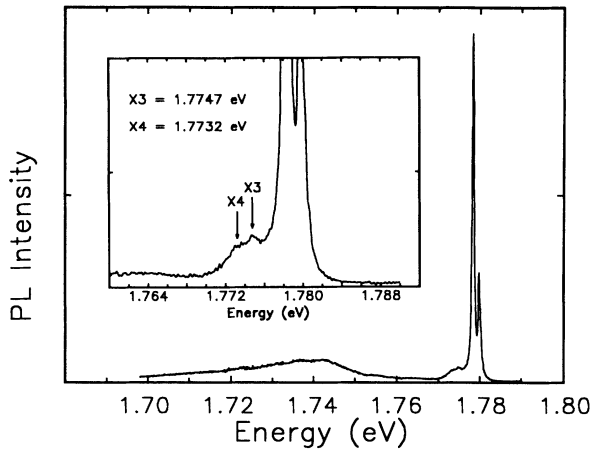

FIG. 2. Typical photoluminescence spectrum of a fresh high-quality GaTe crystal grown by the iodine transport reaction technique. The inset shows two small features, X_3 and X_4, on the low-energy side of the triplet exciton peak.

Figure 3 shows typical polarization-dependent PL results at temperature $T\sim6.4$ K and laser excitation intensity $P\sim0.65$ W/cm^2. The peak at X_1 is strongly polarized perpendicular to the crystal b axis, whereas the peak at X_2 is partially polarized along the b axis. By analogy with GaSe, we assign X_1 and X_2 to the $1S$ ground-state singlet and triplet excitonic emission peaks, respectively.[14,17,18] These peaks are separated by ~1.6 meV, which is comparable to the typical $1S$ singlet-triplet energy sep-

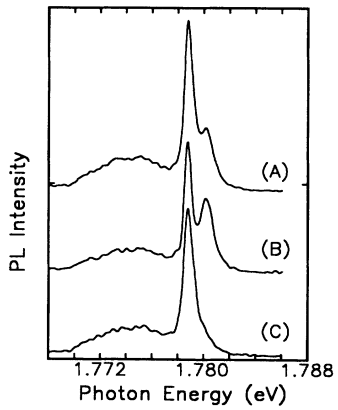

FIG. 3. Typical polarization spectrum of luminescence from GaTe at temperature $T\sim6.4$ K and laser excitation intensity $P\sim0.65$ W/cm^2. (A) No analyzer, (B) $\mathbf{b}\perp$ analyzer, (C) $\mathbf{b}\parallel$ analyzer. Note that the spectra have been shifted relative to each other by a constant value and that intensities for spectra with analyzer have been multiplied by 2 in order to compensate for intensity loss due to the analyzer.

aration of 2 meV in GaSe.[14] The intensity ratio of the observed $1S$ triplet and singlet excitonic emission peaks in GaTe is close to the 3:1 ratio of their spin multiplicities.

In the better-known compound GaSe, the ground-state exciton is split into singlet and triplet states by the electron-hole exchange interaction,[14,18] and the $1S$ singlet exciton emission is strongly polarized perpendicular to the crystal layer plane, i.e., parallel to its Ga—Ga bond direction. In GaTe, however, the singlet emission is strongly polarized perpendicular to the crystal b axis, with a large component in the crystal cleavage plane, and almost parallel to the "new" Ga—Ga bonds. The linearly polarized emission indicates alignment and orientation of singlet excitons, whose radiative lifetime is less than, or comparable with, their spin-relaxation time.

In the electric-dipole approximation, an exciton that is initially created by a photon is a singlet, while transition to the triplet state is allowed in GaSe if weak spin-orbit interaction, which induces inter-valence-band mixing, is considered. This interpretation in terms of weak spin-orbit coupling gives a good description of the multiplet nature of exciton states in III-VI layered semiconductor compounds, and singlet and triplet exciton spectra due to a considerable exchange splitting of the exciton ground state are indeed observed; however, it should be noted that the discussion of singlet and triplet states is not strictly rigorous, since a small spin-orbit interaction is required.[14,18]

PL measurements were also made on a thin flake sample that was bent into a "bridge" form, in order to observe strain-induced effects. In Fig. 4, the resulting spectrum is compared with that from an unstrained crystal. The singlet and triplet peaks X_1 and X_2 appear at about the same energies, and the other two peaks X_3 and X_4, at energies 1.7757 and 1.7735 eV, have greater intensities in the deformed sample than in the undeformed one. Strain is believed to introduce a defect center in GaTe, and peaks X_3 and X_4 are assigned to the singlet (X_1) and triplet (X_2) exciton states bound to this defect center, respectively.

Figure 5 shows typical transmission spectra for GaTe

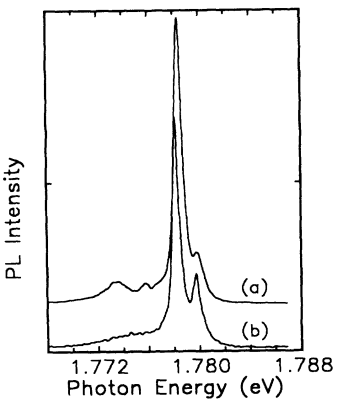

FIG. 4. Comparison of photoluminescence spectra from (a) an intentionally slightly deformed GaTe sample and (b) an unstrained sample, at temperature $T \sim 6$ K and laser excitation intensity $P \sim 5.3$ W/cm^2, showing the effect of strain.

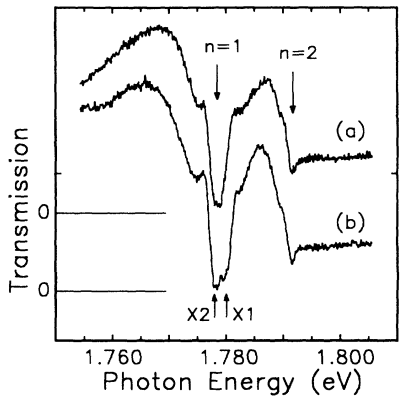

FIG. 5. Typical normalized transmission spectra of GaTe at $T=2$ K. The upper curve (a) corresponds to **E**$\|$**b** and the lower curve (b) corresponds to **E**$\perp$**b**, for which the $n=1$ free-exciton peak is barely resolved into a doublet consisting of two peaks X_1 and X_2. The $n=2$ absorption feature is also indicated.

near the band-gap energy E_g, at $T=2$ K. The fundamental absorption edge appears at $E_g \approx 1.794$ eV for both **E**$\|$**b** and **E**$\perp$**b** polarizations. The $n=1$ exciton peak is observed at 1.7786 eV, with a FWHM of ~ 2.1 meV for unpolarized light. There is a clear difference between the shapes of the $n=1$ absorption peak (transmission minimum) for polarization parallel and perpendicular to the b axis. For **E**$\perp$**b**, this peak is barely resolved into a doublet, which we label X_1 and X_2 in accordance with the luminescence results. The reduction in absorption on the high-energy side of the peak observed for **E**$\|$**b** strongly suggests a doublet, of which the X_1 state is created only when the incident light has a component **E**$\perp$**b**.

The transmission spectra are in agreement with the luminescence results in that the singlet X_1 is created only for incident light polarized perpendicular to the b axis. Both creation and recombination of the singlet peak X_1 satisfy the same selection rule.

Since the polarization direction of creation and recombination of X_1 is parallel to the "new" Ga—Ga bonds that lie approximately in the layer plane, we suggest that the singlet exciton may be related to these bonds, which have no counterpart in GaSe, GaS, or InSe, and may make an important contribution to the electronic levels near the band gap of GaTe.[19] In fact, above-gap excitations at energies of 2.14,[20] 1.87, 1.96, 2.15, 2.395, 2.485, and 2.565 eV (Ref. 21) have been observed only for polarization **E**$\perp$**b** in the plane of the layer, and are forbidden when **E**$\|$**b**, a result which has also been attributed to the "new" Ga—Ga bonds.[11]

Besides the $n=1$ ground-state free exciton, other features apparent in each of the traces of the transmission spectra of Fig. 5 are the $n=2$ exciton at energy 1.7915 eV (which somewhat obscures the band edge), and a weak absorption feature just below the $n=1$ exciton, at energy 1.775 eV. No detectable narrowing effect or polarization dependence is found for the $n=2$ excited-state exciton, so the exchange splitting is appreciable only in the ground state. In fact, the energy separation between the singlet and triplet excitons is essentially equal to the total

exchange energy, which decreases as $1/n^3$ with increasing n.[14]

The effective Rydberg of the ground-state exciton calculated from the values of the energy positions of $n=1$ and 2 excitons in GaTe for a three-dimensional model is ~ 17 meV, with a band gap of 1.7958 eV at helium temperature. The weak absorption feature at 1.775 eV appears at the same energy as the weak X_3 and X_4 defect-related emission peaks observed in the strained GaTe sample (Fig. 4).

From the value of the above-band-gap absorption coefficient in GaTe, Camassel *et al.*[11] estimate the interband transition matrix element $P_{\perp}^2=2.8$ eV. This relatively small value supports a forbiddenlike scheme for the interband transition. A qualitative comparison with GaSe and InSe shows a greater interband transition strength for GaTe, which can be accounted for by the larger atomic spin-orbit splitting of Te atoms (1.10 eV) as compared with Se (0.48 eV).[22] In GaTe, the interband transition strength for **E** parallel to the crystal layer plane is therefore stronger than that for GaSe or InSe.

IV. CONCLUSIONS

We have studied luminescence and transmission spectra of layered GaTe crystals grown by the iodine transport reaction technique. Fresh samples exhibit strong, narrow, well-defined exciton lines near the band edge. The sharp doublet peak observed in photoluminescence spectra just below the band gap is attributed to the ground-state $1S$ singlet and triplet excitons. The higher-energy singlet emission peak is strongly polarized perpendicular to the b axis, and is independent of the polarization of the exciting radiation. This polarization dependence is consistent with that observed in transmission spectra, which show that the higher-energy exciton state is created only for incident light which has a component $\mathbf{E}\perp\mathbf{b}$. The polarization direction for creation or recombination of the singlet is approximately parallel to the "new" Ga—Ga bonds in GaTe that lie approximately in the layer planes and have no counterpart in GaSe, GaS, and InSe. The triplet exciton transition is related to the inter-valence-band mixing induced by weak spin-orbit coupling, which is larger than that in GaSe crystals. In order to substantiate further the explanation in terms of $n=1$ singlet and triplet excitons in GaTe, magnetoabsorption experiments[14] need to be done.

Free-exciton linewidths give tentative criteria for evaluation of the crystal quality. The very narrow linewidths of exciton emission lines presented in this paper show that the fresh samples of GaTe crystals grown by iodine transport reaction are of high quality. The singlet and triplet exciton structure is well resolved. By contrast, the reported results on melt-grown GaTe indicate a higher impurity and defect content. The exciton singlet and triplet linewidths are inhomogeneously broadened and mixed, giving rise to a broad exciton peak.[9,11] This suggests that vapor-grown GaTe samples are of higher quality. Also worthy of note is the degradation of our samples with use. After several weeks and many helium-run thermal cycles, both the emission and absorption exciton lines were broadened, although after our samples were exposed to atmospheric contamination for about one year we observed no change in the color of crystal surfaces as Camassel *et al.*[10] did in samples from melt growth.

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