Stacking-fault excitons in AgBr microcrystals with twin planes

Alfred Marchetti

Kodak Research Laboratories, 1999 Lake Avenue, Rochester, New York 14652-4708
and Center for Photoinduced Charge Transfer, University of Rochester, Rochester, New York 14627
(Received 23 December 1993; revised manuscript received 23 June 1994)

The visible emission and excitation spectra of AgBr microcrystals containing single and parallel double twin planes have been obtained. A band at 462.28 nm (2.6813 eV) is observed in the excitation spectrum. This feature is about 2.5 meV below the indirect exciton band edge. Coincident emission features are observed. The band in the excitation spectrum of microcrystals with two parallel twin planes is often split into a doublet with splittings between 1 and 2 meV. The new band is assigned to an exciton created at a stacking fault and the splittings are thought to be due to tunneling of the exciton between proximate twin planes. The small binding energy of the exciton to the twin plane is in accord with the very small strain field about a twin plane.

INTRODUCTION

Twin planes are a subset of defects known as stacking faults.[1] In cubic crystals they represent a mirroring in the layer sequence $aBcAbC$ to $aBcA'b'AcBa$. Twinning in fcc, rock salt structures occurs at a {111} plane and can also be viewed as a 60° rotation of one plane with respect to another. Twin planes can have either a cationic or an anionic mirror layer. These features are of pedagogical interest because they represent a symmetry-breaking structure similar in many ways to a surface. They are of industrial importance because they are a feature that engenders tabular or planar growth in silver halide microcrystals used in photographic films. A tabular microcrystal has a larger surface-to-volume ratio than a cubic or octahedral microcrystal allowing more dye to be adsorbed per unit volume and hence more light absorption per unit volume.

Stacking-fault excitons (SFE's) have been observed in BiI_3 and GaSe.[2-4] Both these materials are layered and easily form stacking faults. The SFE's in BiI_3 have been studied extensively, possibly due to the sharp lines that appear in the absorption and emission spectra just below the indirect exciton edge.[2,3] SFE's are expected to exhibit a more two-dimensional nature than their more normal exciton counterparts.[2-4]

AgBr is an indirect-band-gap semiconductor, thus its absorption spectrum is very weak in the region of the indirect exciton band-gap energy (2.6838 eV). The excitonic properties of this material have been studied extensively by emission spectroscopy.[5] Free exciton emission and emission from a number of weakly bound (a few meV) excitons have been observed just below the indirect exciton band gap. Excitation spectroscopy has been used to examine the absorption of AgBr in the region of the indirect band gap.[6] The indirect exciton absorption can be observed by monitoring either the iodide bound exciton emission (500 nm ≈ 2.48 eV) or the donor-acceptor emission (590 nm ≈ 2.10 eV), which contains a contribution from intermediate case exciton (close D-A pairs) recombination.[6,7]

Silver halide microcrystals, when grown in gelatin, nor-

mally have one of two regular morphologies: cubes with {100} faces and octahedra with {111} faces.[8] AgBr microcrystals can also be grown in a tabular morphology with {111} faces and one or more twin planes parallel to the tabular faces.[8] Twin planes have been observed in cryosectioned samples by transmission electron microscopy.[9] In those microcrystals with two parallel twin planes the spacing between twin planes is often between 8 and 20 nm.

In this report we describe absorption and emission features that occur because an exciton is created at twin planes in AgBr. We have examined the excitation spectra of a number of three-dimensional and tabular AgBr microcrystals dispersed in gelatin. We also estimate the binding of an exciton in a weak strain field.

EXPERIMENT

The AgBr microcrystal dispersions were made by standard techniques used for producing silver halide in gelatin dispersions for photographic films.[10,11] These procedures allow the production of cubic, octahedral, and tabular morphologies (with single or double twin planes) by controlling the precipitation conditions. The most important factor is the silver ion activity during nucleation and growth. All the microcrystals produced were examined in a scanning electron microscope. The octahedral microcrystals were monodispersed in size with an octahedral edge length of 320±15 nm. Those dispersions with tabular grains that contained only single twins were > 45% single twins by number count, with the rest being smaller octahedral grains and < 1.5% microcrystals with double twins. The single twin microcrystals were triangular in shape, with an edge length of 330±50 nm. The doubly twinned microcrystals were hexagonal in shape and had a mean thickness of 47±6 nm and an equivalent circular diameter of 800±190 nm. Transmission electron micrographs of Pt/Pd shadowed carbon replicas of the octahedral (O), single twin (ST), and double twin (DT) microcrystals are shown in Fig. 1.

The excitation spectra of these samples were obtained at liquid-helium temperatures ($T \approx 6$ or 2 K), with a con-
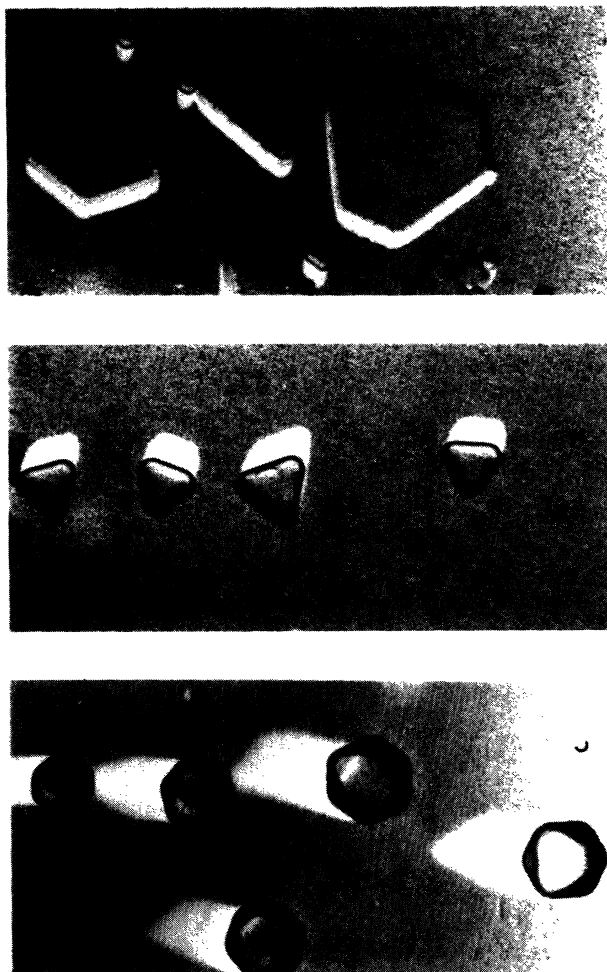
FIG. 1. Transmission electron micrographs of Pt/Pd shadowed carbon replicas of the three types of silver halide microcrystals examined: double twin (DT), single twin (ST), and octahedral (O). The magnification is approximately 30 000.

tinuously tunable dye laser. The dye laser employed coumarin 120 in a glycerol-benzyl alcohol mixture with cyclooctatetraene added to reduce triplet-triplet absorption. The bandwidth of the dye laser emission was 0.12 meV. The dye was pumped by the 351/360-nm uv lines from an argon-ion laser. The rest of the spectroscopic apparatus has been described previously.[12]

RESULTS AND DISCUSSION

Figure 2 shows the excitation and emission spectra for three dispersions of AgBr microcrystals in the region of the indirect exciton band-gap energy $[E_g(ex)]$. These dispersions are composed of octahedral microcrystals, single twin microcrystals, and microcrystals with two parallel twin planes. In these excitation spectra the emission is monitored at 500 nm (iodide bound exciton emission). Similar spectra were obtained when the monitoring wavelength was 600 nm (donor-acceptor emission).[6] Equivalent excitation spectra were obtained on other octahedral and cubic microcrystal dispersions, and no evi-

dence was found for a new band in the excitation spectra. The exciton emission spectra for octahedral and cubic microcrystals differ. These differences reflect the different levels of point defects and impurities that are incorporated into these microcrystals under different growth conditions.

The absorption feature at 2.6813 eV (vacuum corrected), which is associated with microcrystals containing twin planes, is approximately 2.5 meV below the exciton band-gap energy $[E_g(ex)=2.6838$ eV]. The appearance of an additional feature in the excitation spectrum is thought to be caused by the symmetry-breaking effect of the twin plane, which allows the creation of a weakly trapped exciton in the region of a twin plane. The emission spectra for those microcrystals that contain a single twin plane have a 0-0 band at 2.680_8 eV, which is coincident with the absorption feature, and they have a strong TO-phonon band at 2.672_2 eV, with weaker LA- and LO-phonon lines at 2.669_6 and 2.662_9 eV, respectively. Several preparations of microcrystals containing sin-
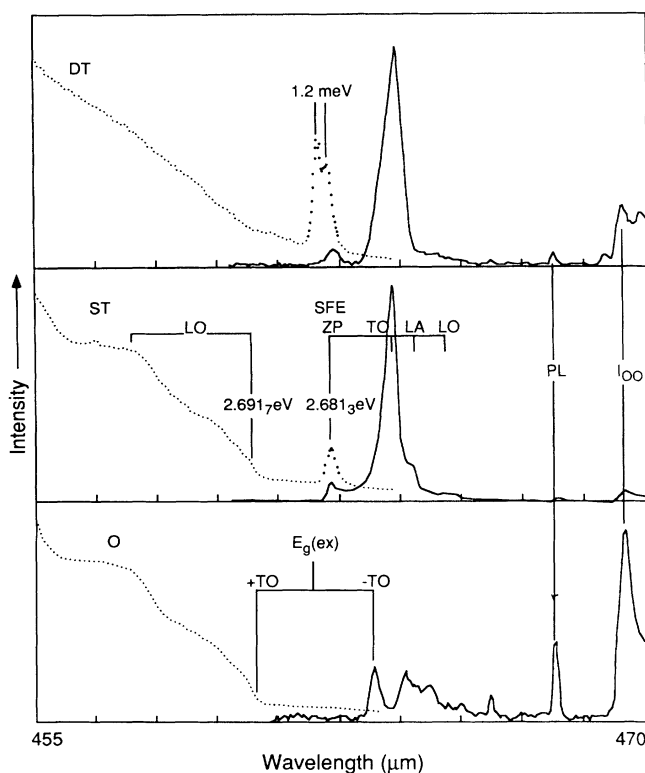

FIG. 2. Excitation (dotted) and emission (solid) spectra of double twinned (DT), single twinned (ST), and octahedral (O) AgBr microcrystals at 6 K. The monitoring wavelength was 500 nm. The feature associated with exciton localization at a twin plane is at 462.28 nm. The zero phonon (ZP) and phonon replicates (TO, LA, and LO) are identified for the SFE emission from the single twin (ST) microcrystals. The broad higher-energy peaks in the excitation spectra are due to LO-phonon scattering. The splitting in the excitation spectrum of the DT microcrystal is 1.2 meV. The 0-0 band of the iodide bound exciton (I_{00}) and a plasma line (PL) used for calibration are indicated.

gle twin planes and double twin planes were examined. All microcrystals examined that contained twin planes exhibited the new band in the excitation spectrum.

The exciton wave function in AgBr is a product of valence-band (L point $[L_4^-, L_5^-]$) and conduction-band (Γ_6^+) wave functions.[13,14] In the absence of exchange there are four degenerate states: two are of pure triplet character and two are of mixed singlet-triplet character. Exchange interactions split this into two doubly degenerate pairs with the pure triplets lower in energy. The exchange energy has been estimated by magnetoabsorption (0.33 meV) and more recently by Raman scattering (0.17 meV) and quantum beat spectroscopy (0.13 meV).[13,14] With absorption and emission linewidths > 1.0 meV, the exchange splitting is not observed.

Some of the microcrystals containing two parallel twin planes exhibit a doublet in their excitation spectrum. The example shown in Fig. 2 has a splitting of 1.2 meV. This splitting, when observed in other double twin preparations, ranged from 1 to almost 2 meV. The average energy of the two lines (2.681_4 eV) is the same as the energy of the line in the single twin preparations. The lines of the doublet in the excitation spectrum of the DT preparation shown in Fig. 2 are of unequal intensity, other preparation exhibit doublets of approximately equal intensity. A band in the emission spectrum is coincident to the lower component in the excitation spectrum. The coincident band in the emission spectrum of the DT preparation (Fig. 2) broadens from 1.3 to 2.0 meV [full width at half maximum (FWHM)] as the temperature was raised from 2 to 12 K. The upper component is allowed (see Fig. 2) and becomes more populated at higher temperatures. The splitting of the new feature in AgBr tabular microscrystals with double twin planes is assigned to tunneling of an exciton between wells (the excitons oscillating between two closely spaced twin planes). Estimates for the tunneling splitting of a particle in coupled square wells of several nm width and separated by ≈ 10 nm are on the order of a few meV. The observed splittings are in qualitative agreement with what we have observed about the twin plane separation in various preparations; that is, larger average separations have smaller splittings.

Electrons, holes, and excitons can be bound at structural lattice defects because the associated strain field causes a perturbation of the conduction- and valence-band energies in the region of the defect.[15] In accessing the effect that a twin plane may have on charge carriers or excitons, it will be assumed that the binding region is large compared to a lattice constant, making the effective mass and continuum approximation appropriate. It will be shown that the binding energy at a structural defect will be small compared to the exciton binding energy, and that the binding of only one carrier will be large and the major source of binding for an exciton. The strain field at a twin plane is assumed to be one dimensional with its direction perpendicular to the twin plane (and thus parallel to the [111] direction). The binding energy of a carrier at an edge dislocation has been calculated by variational methods using the potential induced by the strain and the effective-mass approximation, and assuming a parabolic band. Various starting wave func-

tions have been tried, and all lead to similar expressions for the binding energy.[16-18]

The Hamiltonian for a single electron (hole) in a strain $[\varepsilon(r)]$ is given in Eq. (1),

$$\mathcal{H} = p^2/2m^* + \Sigma_{ij} D_{ij} \varepsilon_{ij}(r) , \tag{1}$$

where p is the momentum, D_{ij} is the set of deformation potentials, and m^* is the effective mass.[17] If it is assumed that there is a small dilation (δ) near a twin plane, and that it is perpendicular to the plane, this becomes a one-dimensional problem and Eq. (1) becomes

$$\mathcal{H} = \frac{p^2}{2m^*} + D\varepsilon_{xx} \Longrightarrow \frac{\hbar^2 \nabla^2}{2m^*} + \frac{D\delta}{|x|} . \tag{2}$$

The resultant second-order differential equation can be recast, with substitutions, to the following form:[19]

$$\frac{d^2\Psi}{d\eta^2} + \left[\frac{1}{|\eta|} - \lambda^2\right]\Psi = 0 . \tag{3}$$

The solution to this one-dimensional differential equation requires a wave function which goes to zero at $x = 0$ and ∞. The solutions are doubly degenerate and for the $n = 1$ level are of the form[20]

$$\Psi_{1^-}(\eta) = c_1(1)\eta e^{-\frac{|\eta|}{2}} , \quad \Psi_{1^+}(\eta) = c_1(1)|\eta|e^{-\frac{|\eta|}{2}} . \tag{4}$$

For $n > 1$ the wave functions are more complex. The energy is given by

$$E_n = -\frac{m^*(D\delta)^2}{\hbar^2 n^2} . \tag{5}$$

Surfaces of silver halide materials were predicted by atomistic simulations to rumple and surface-extended x-ray-absorption fine-structure (SEXAFS) measurement are in accord with this prediction.[21] Atomistic simulation indicates that the anion twin plane is more stable in AgBr, and that the first cation sublattices on either side shift ≈ 0.03 A away from the twin plane.[22] This shift, 0.03 A, is the effective dilation at twin plane. Substituting the values for the deformation potentials [-2.3 eV (e^-); 0.7 (h^+) to -3.8 (h^+)], and effective mass [$m_e^* - 0.2897$, $m_h^* = 1.71(\|)$], Eq. (5) predicts that an electron will be bound to a twin plane by 0.2 meV and that a hole may be repelled or bound by as much as 2.9 meV depending on constants used.[23,24] Thus the expected stabilization of an exciton is at most ≈ 3 meV assuming that the stabilization comes from binding the hole. This is in accord with the magnitude of the observed binding energy.

The fact that the stacking-fault-related absorption is observed in excitation spectra by monitoring either the iodide bound exciton emission at 500 nm or the D-A emission at 600 nm indicates these excitons are detrapped or that they migrate to iodide ions and D-A pairs on the twin plane. Examination of Fig. 2 in the region of the iodide bound exciton 0,0 band (≈ 470 nm) reveals two additional emission peaks about 2.4 meV above and below this band for the DT microcrystal. Examination of the emission spectra of other microcrystal dispersions reveals that emission lines associated with the iodide bound exciton only occur in those microcrystals with twin planes.

Emission lines, due presumably to recombination of excitons on iodide ions at or on the twin plane, are not always observed in twin-plane-containing microcrystals. Their intensity is dependent on the inadvertent iodide concentration which varies from about 50 to 2500 mppb as estimated from emission intensity ratios.[25] If it is assumed that only iodides on the twin plane or in the next anion layer will be influenced by the strain field enough to cause additional emission lines, then at the lowest iodide concentration microcrystals 300×300 nm^2 will have only a 5% probability of having an iodide associated with the twin plane. Thus it is concluded that while weak iodide bound exciton emission lines are observed in microcrystals with twin planes, most of the excitons rapidly escape the twin plane at liquid-helium temperatures. The measured trap depth of an exciton at a twin plane (2.5 meV), and a preexponential factor of 10^{11} gives an estimated mean release time of ≈ 1 ns.[26]

Finally the structure that is observed in the higher-energy region of the excitation spectra (see Fig. 2) and is assigned to LO-phonon scattering is absent in the thin (47-nm) double twin (DT) dispersion. The absence of a LO-phonon-scattering structure may be caused by confinement effects in which the dominant loss of energy for an exciton with excess translational energy will be scattering from the surfaces as opposed to phonon scattering.[6,12] This loss of LO-phonon involvement has been observed in nanocrystals (10-nm diameter) fabricated in reverse micelles.[27]

ACKNOWLEDGMENTS

[1] W. Bollmann, *Crystal Defects and Crystalline Interfaces* (Springer-Verlag, New York, 1970), Chap. 3.

[2] M. Ichida, T. Karasawa, and T. Komatsu, Phys. Rev. B **47**, 1474 (1993), and references cited.

[3] K. Watanabe, T. Karasawa, T. Komatsu, and Y. Kaifu, J. Phys. Soc. Jpn. **55**, 897 (1986).

[4] Y. Sasaki and Y. Nishina, Physica **105B**, 45 (1981), and references cited therein.

[5] W. von der Osten and H. Stolz, J. Phys. Chem. Solids **51**, 765 (1990).

[6] M. Timme, E. Schreiber, H. Stolz, and W. von der Osten, J. Lumin. **55**, 79 (1993).

[7] A. P. Marchetti, M. S. Burberry, and J. P. Spoonhower, Phys. Rev. B **43**, 2378 (1991).

[8] R. C. Baetzold and C. R. Berry, in *Theory of the Photographic Process*, 4th ed., edited by T. H. James (Macmillan, New York, 1977), Chap. 1-II.

[9] R. V. Mehta, R. Jagannathan, and J. A. Timmons, J. Imag. Sci. Technol. **37**, 127 (1993).

[10] C. R. Berry, in *Theory of the Photographic Process* (Ref. 8), Chap. 3.

[11] A. K. Tsaur *et al.*, U.S. Patents Nos. 5147771 (15 September 1992), 5147772 (15 September 1992), 5147773 (15 September 1992), 5171659 (15 December 1992), and 5210013 (11 May 1993).

[12] A. P. Marchetti, K. P. Johansson, and G. L. McLendon, Phys. Rev. B **47**, 4268 (1993).

[13] M. Matsushita, J. Phys. Soc. Jpn. **35**, 1688 (1973).

[14] W. von der Osten, in *Light Scattering in Solids VI*, edited by M. Cardona and G. Guntherodt (Springer-Verlag, New York, 1991), Chap. 7.

[15] J. I. Pankove, *Optical Processes in Semiconductors* (Dover, New York, 1971).

[16] V. Celli, A. Gold, and R. Thomson, Phys. Rev. Lett. **8**, 96 (1962).

[17] P. R. Emtage, Phys. Rev. **163**, 865 (1967).

[18] Yu. T. Rebane and Yu. G. Shreter, in *Polycrystalline Semiconductors II*, edited by J. H. Werner and H. P. Strunk (Springer-Verlag, New York, 1991).

[19] With another variable transformation Eq. (3) is the same as the familiar radial part of the hydrogen atom.

[20] J. Hamilton and D. Ross (private communication).

[21] Y. T. Tan, K. J. Lushington, P. Tangyunyong, and T. N. Rhodin, J. Imag. Sci. Technol. **36**, 118 (1992).

[22] R. Baetzold (private communication) and (unpublished).

[23] W. von der Osten, in *Semiconductors. Physics of II-VI and I-VII Compounds, Semimagnetic Semiconductors*, edited by O. Madelung, Landolt-Börnstein, New Series, Group 3, Vol. 17, Pt. b (Springer, Berlin, 1982), p. 273ff.

[24] Experimental values of the deformation constant appropriate to the valence band are positive but they are difficult to obtain and vary widely among experimenters. Thus a calculated value taken from S. Ves, D. Glotzel, M. Cardona, and H. Overhof, Phys. Rev. B **24**, 3073 (1981), is also used.

[25] F. Moser and S. L. Lyu, J. Lumin. **3**, 447 (1971).

[26] The preexponential factor of 10^{11} was chosen because carriers trapped in strain fields are thought to be coupled strongly to the lattice; see Ref. 18.

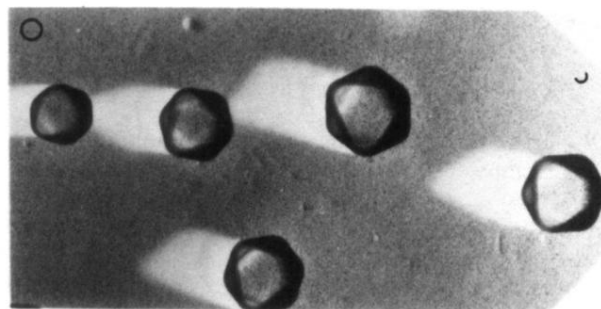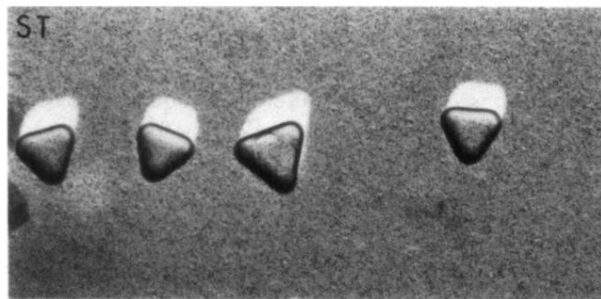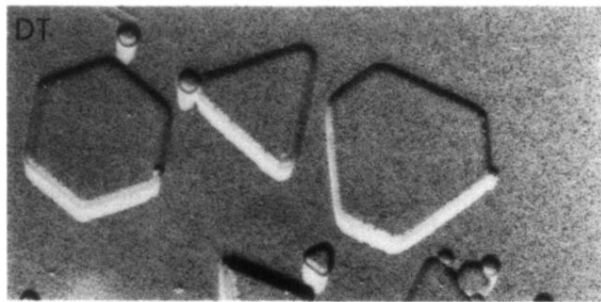[27] A. P. Marchetti, W. Chen, and G. L. McLendon (unpublished).

FIG. 1. Transmission electron micrographs of Pt/Pd sha-
dowed carbon replicas of the three types of silver halide micro-
crystals examined: double twin (DT), single twin (ST), and octa-
hedral (O). The magnification is approximately 30 000.