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# Fabrication and optical properties of ultrathin CdSe filaments incorporated into the nanochannels of fibrous magnesium silicates

V V Poborchii<sup>†‡</sup>, V I Al'perovich<sup>‡</sup>, Y Nozue<sup>§</sup>, N Ohnishi<sup>†</sup>, A Kasuya<sup>†</sup> and O Terasaki<sup>§</sup>

<sup>†</sup> Institute for Materials Research, Tohoku University, Katahira, Sendai 980-77, Japan

<sup>‡</sup> Ioffe Physico-Technical Institute, St Petersburg 194021, Russia

<sup>§</sup> Department of Physics, Graduate School of Science, Tohoku University, Sendai 980-77, Japan

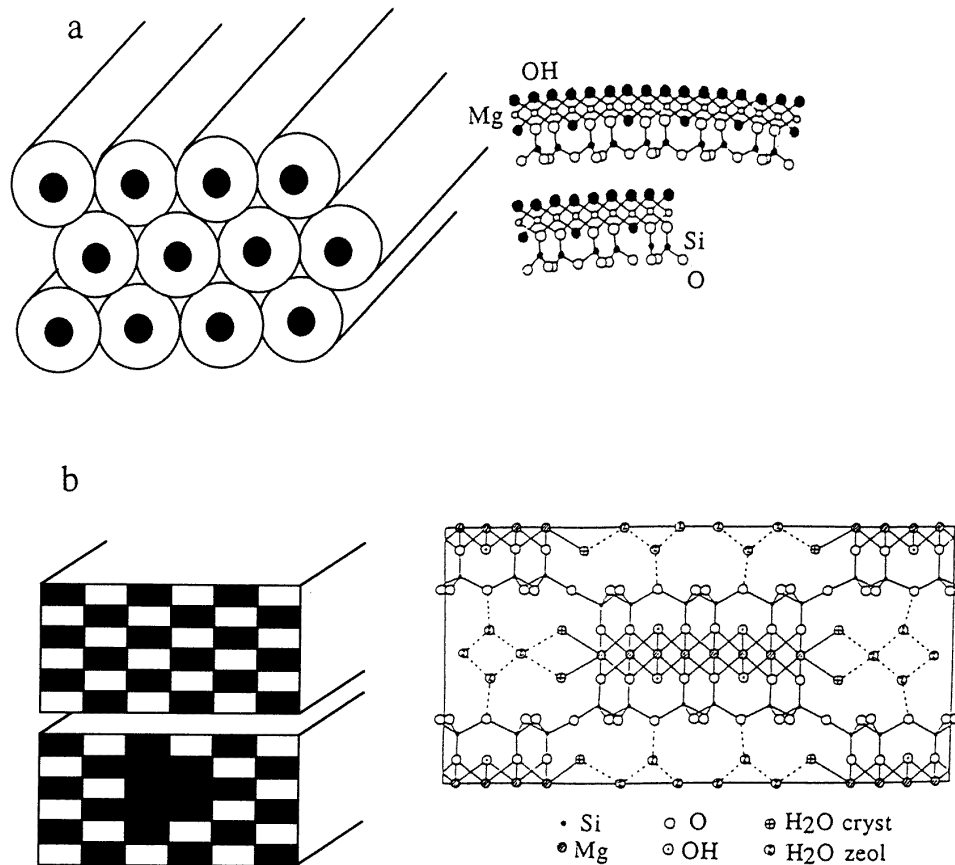
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**Abstract.** CdSe has been synthesized in the nanochannels of the transparent fibrous magnesium silicates, namely chrysotile asbestos and sepiolite. The optical absorption spectra of CdSe confined in both matrices have been found to display a blue shift compared with bulk CdSe (about 0.14 eV for asbestos, and about 0.9 eV for sepiolite) and a strong polarization dependence. CdSe filaments with diameters 7–8 nm inside asbestos channels have been observed by transmission electron microscopy. Resonance Raman bands due to the LO phonon of CdSe filaments have been found, when the incident and scattered light are polarized along the filaments. Asbestos-confined CdSe filaments are considered as cylindrical quantum wires, which display a quantum size effect in the electron spectrum. The interpretation of the absorption spectra of the sepiolite-confined CdSe is more speculative. One possibility is the formation of CdSe filaments with diameters about about 3 nm in mesochannels of the sepiolite.

## 1. Introduction

Semiconducting quantum wires incorporated into nanochannels of transparent dielectric matrices are interesting for physical studies and potential applications because of a number of advantages compared with quantum wires prepared by traditional methods such as molecular beam epitaxial growth of the systems GaAs–AlGaAs. These advantages give the possibility of preparing a large number of the wires with diameters of a few nanometres, the possibility of direct measurements of the linear and non-linear optical absorption in a wide spectral region, accessibility to many different materials, the bulk character of samples containing this kind of quantum wire, etc.

Recently a variety of semiconducting ultrathin filaments (real quantum wires) inside chrysotile asbestos nanotubes has been prepared by means of the injection of molten materials into the asbestos channels and examination by optical spectroscopy [1–3]. A high absorption anisotropy has been observed for the asbestos-containing wires. A strong quantum size effect has been found for GaAs wires of 6 nm diameter [1, 2]. A strong and fast third-order optical nonlinearity has been found for this type of wire [4]. However, the method of injection of a liquid material into channels cannot be applied for the materials with melting temperature higher than about 1000 °C. The asbestos-confined semiconducting quantum wires of such materials should be prepared by other methods.



**Figure 1.** Channel and atomic structures of (a) chrysotile asbestos and (b) sepiolite. The defect structure responsible for the formation of the mesochannels is shown for the sepiolite.

In this work, CdSe has been synthesized for the first time inside channels of chrysotile asbestos and sepiolite. Both asbestos and sepiolite containing CdSe (asb-CdSe and sep-CdSe, respectively) have been characterized by polarized optical absorption spectroscopy. Asb-CdSe has been characterized in more detail by transmission electron microscopy (TEM) and polarized Raman spectroscopy.

## 2. Experimental details

The chrysotile asbestos (composition,  $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$ ) is a fibrous magnesium silicate consisting of closely packed parallel tubes with external diameters 20–30 nm and with internal diameters 2–10 nm (figure 1(a)). The sepiolite is also fibrous magnesium silicate (composition,  $\text{Mg}_8\text{Si}_{12}\text{O}_{30}(\text{OH})_4$ ), but sepiolite channels are unisized intracrystalline cavities with cross section 1.1 nm $\times$ 0.56 nm. The crystalline and channel structures of the sepiolite are shown in figure 1(b). Detailed descriptions of the structures have been given in [5] for chrysotile asbestos and in [6] for sepiolite.

We used a natural asbestos of Uzbek origin and natural sepiolite of Chinese origin. CdSe was synthesized in the channels by means of the following procedure. In the first step, a water solution of  $\text{Cd}(\text{COOH})_2$  was introduced into the channels at a temperature of about  $100^\circ\text{C}$  and a pressure of about 1 kbar and, in the second step after drying, the specimen was treated with  $\text{H}_2\text{Se}$  vapour at a temperature of about  $450^\circ\text{C}$ , according to the chemical reaction  $\text{Cd}(\text{COOH})_2 + \text{H}_2\text{Se} = \text{CdSe} + 2\text{HCOOH}$ . Then the samples were heated in vacuum to a temperature of  $450\text{--}500^\circ\text{C}$  to remove excess selenium. The procedure can be repeated several times to increase the loading density of CdSe. However, it is difficult to fill all the free space of the channels. In our estimation, the volume fraction of CdSe in asb-CdSe is less than  $10^{-3}$ .

TEM observation was made using a 400 kV JEM-4000EX electron microscope equipped with a slow-scan CCD camera. The specimens were crushed to obtain separate fibres and deposited on a holey carbon film. TEM images were taken under a low-dose condition using a CCD camera. The asbestos channels were observed clearly, but the observation of the sepiolite channels was found to be much more difficult.

Optical absorption spectra were studied using a microspectrophotometer equipped with reflection-type micro-objectives and a standard single monochromator with changeable gratings. Because of the fibrous structure, the specimens display significant surface light scattering. The specimens were immersed in a liquid consisting of 90% glycerol and 10% water with a refraction index close to that of asbestos or sepiolite to decrease surface light scattering, the light probe size being  $10\text{--}50\ \mu\text{m}$ .

Raman spectra were studied in the back-scattering geometry using a DFS-24 double monochromator equipped with a microscope, the He-Ne laser 632.8 nm line light probe size being about  $10\ \mu\text{m}$ .

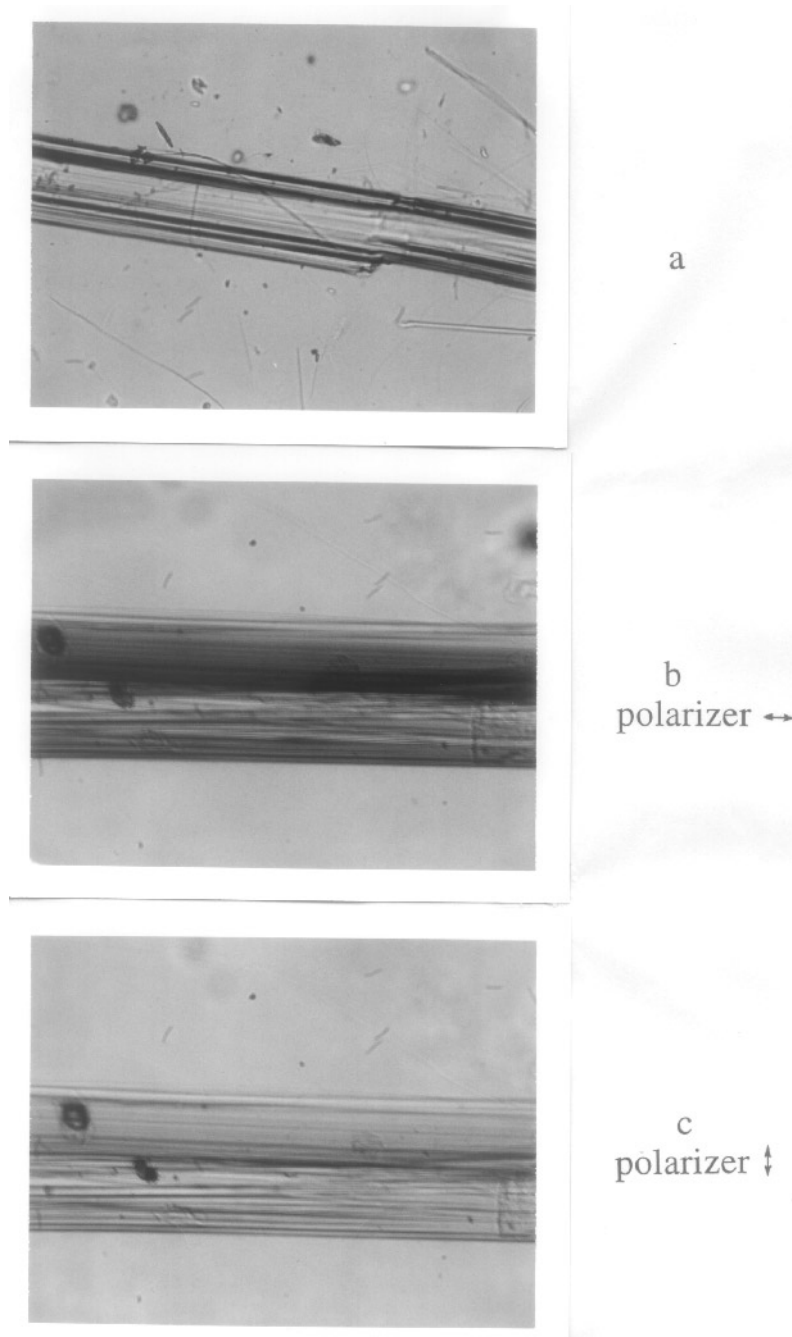
### 3. Results and discussion

Transparent asbestos (figure 2(a)) after the incorporation of CdSe displays a red colour for light polarized along the channels ( $E \parallel c$ , where  $c$  is the channel direction) and a yellow colour for light polarized perpendicular to the channels ( $E \perp c$ ). In the black-and-white photograph the asb-CdSe sample for  $E \parallel c$  (figure 2(b)) looks significantly darker than the same sample for  $E \perp c$  (figure 2(c)).

A TEM image of the separated asb-CdSe is shown in figure 3. Dark contrast regions inside channels of diameters  $7\text{--}8\ \text{nm}$  are clearly seen. They are regarded as CdSe filaments because of the large difference between the average scattering amplitude and that of the asbestos matrix. The distribution of the lengths of the wires is quite wide ( $10\text{--}100\ \text{nm}$ ).

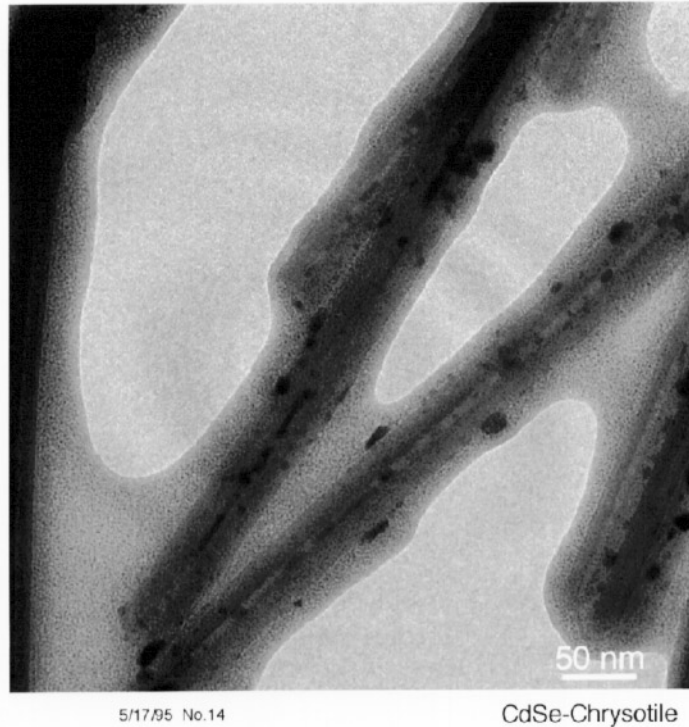
The formation of CdSe filaments in asb-CdSe is supported by the Raman data (figure 4). The spectra for two polarizations were studied. Firstly the incident and scattered light were polarized along the channels ( $cc$  polarization); secondly the incident and scattered light were polarized perpendicular to the channels and parallel each other ( $aa$  polarization, where  $a$  is the direction perpendicular to the channels). The band strongly polarized along channels at the characteristic frequency of LO phonon of the bulk CdSe, about  $209\ \text{cm}^{-1}$ , and its overtone were observed. It should be noted that the Raman bands of the asbestos are much weaker than the CdSe bands. However, the asbestos displays some structureless luminescence which contributes to the background in the spectra presented in figure 4.

Polarized absorption spectra of asb-CdSe are shown in figure 5. The spectra display higher absorption for light polarized parallel to the channels ( $E \parallel c$ ) and lower absorption



**Figure 2.** Transmission light photographs of (a) pure asbestos and (b), (c) asb-CdSe for polarizations of the light (b) parallel and (c) perpendicular to the asbestos channels.

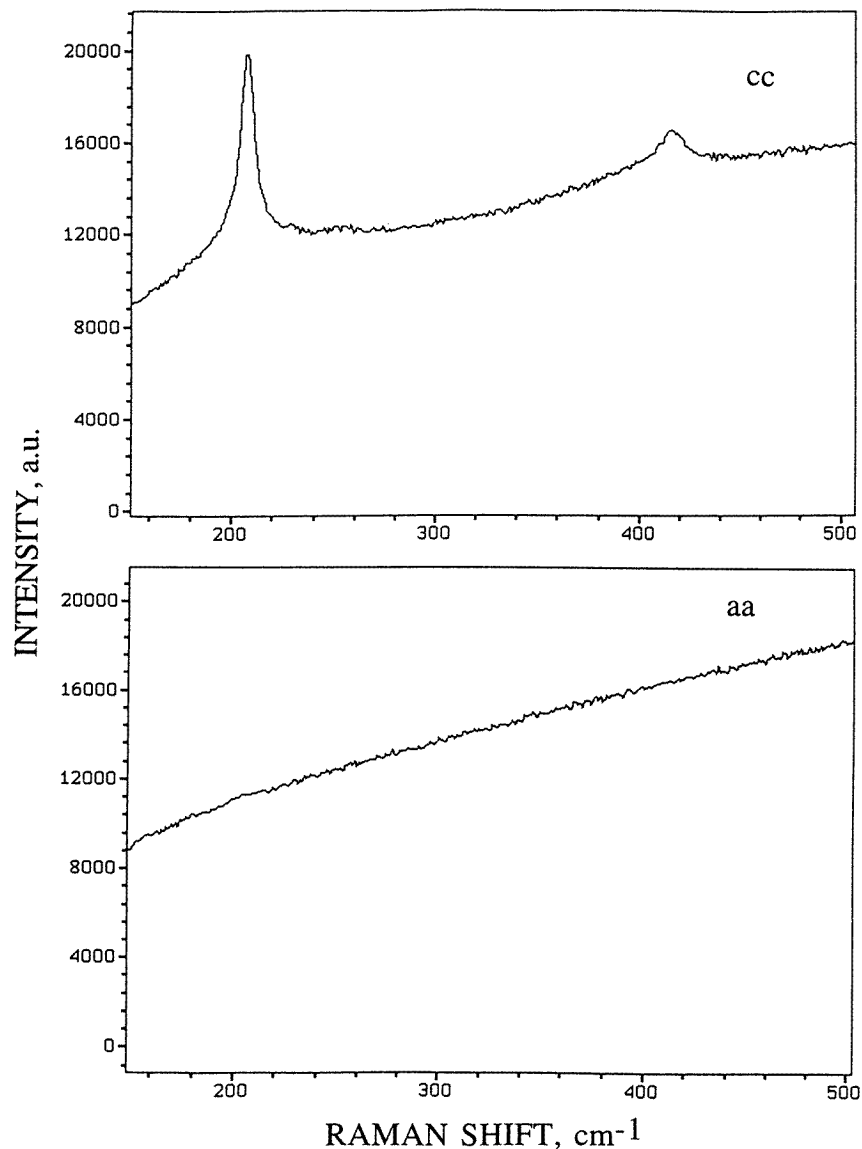
for light polarized perpendicular to the channels ( $E \perp c$ ). An increase in the loading density of CdSe does not effect the shape of the spectra, as only the optical density is increased.



**Figure 3.** TEM image of mechanically separated chrysotile asbestos fibres with CdSe inside channels.

Absorption anisotropy for the asbestos containing wires of different materials (GaAs, InSb, Bi, Hg, Se, Te and CuCl) has been observed earlier [2,3] and explained in terms of the extended Maxwell-Garnet theory [7] for cylindrical wires immersed into the insulating medium, attention being paid to the different values of depolarization factors for light polarized parallel and perpendicular to the cylinder axis. The absorption anisotropy of asb-CdSe can be explained in the same manner. A noticeable background in the spectra is partly attributed to the surface light scattering.

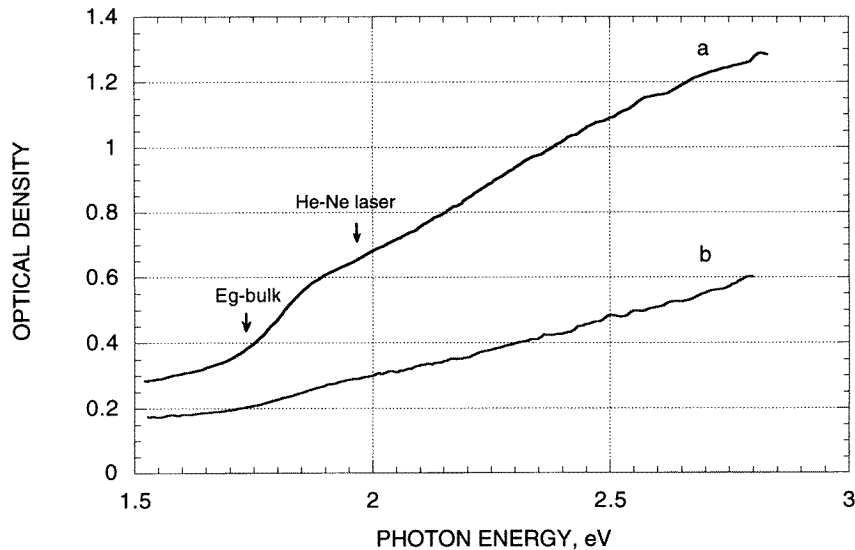
The broad band with the maximum at about 1.87 eV can be attributed to the intersubband transitions of the cylindrical CdSe quantum wires. This band displays a blue shift compared with the bulk CdSe absorption edge (the energy gap of the bulk CdSe is  $E_g \approx 1.73$  eV at room temperature). The assignment of this band to the transitions between quantum-sized valence and conduction subbands can be supported by the calculations. The quantum-sized energy shift of the first intersubband transition in the cylindrical CdSe quantum wires is determined mainly by the energy shift  $\Delta E$  of the conduction subband, because the effective mass  $m_e$  of the electron is significantly smaller than the effective mass of the holes. According to the effective-mass approximation of the size quantization of the electrons in the cylindrical quantum wires with infinite band-gap discontinuity [8],  $\Delta E = \hbar^2 k_0^2 / 2m_e$ , where  $k_0$  is the radial momentum of the electron in the first conduction subband, which is determined from the boundary condition  $J_0(k_0 r_0) = 0$  ( $J_0$  is the Bessel function and  $r_0$  is the radius of the wire). For  $m_e = 0.12m_0$  and  $r_0 = 3.5$  nm,  $\Delta E \simeq 0.15$  eV; for  $r_0 = 4$  nm  $\Delta E \simeq 0.11$  eV. Good agreement between the calculated and experimental values of the



**Figure 4.** Raman spectra of asb-CdSe for the polarizations of the incident and scattered light parallel to each other and parallel to the channels (*cc* polarization) and perpendicular to the channels (*aa* polarization) (a.u., arbitrary units).

shift can be considered as an argument for accessibility of the cylindrical quantum wires model for asb-CdSe and for the quite correct determination of the average wire radius from the TEM image.

The high intensity of the 209 cm<sup>-1</sup> Raman band of the CdSe LO-phonon and its overtone for the *cc* polarization is associated with the resonance Raman scattering through the interband electron transitions polarized along the channels. The photon energy of 1.959 eV for the He-Ne laser line of 632.8 nm corresponds well to the absorption region of the



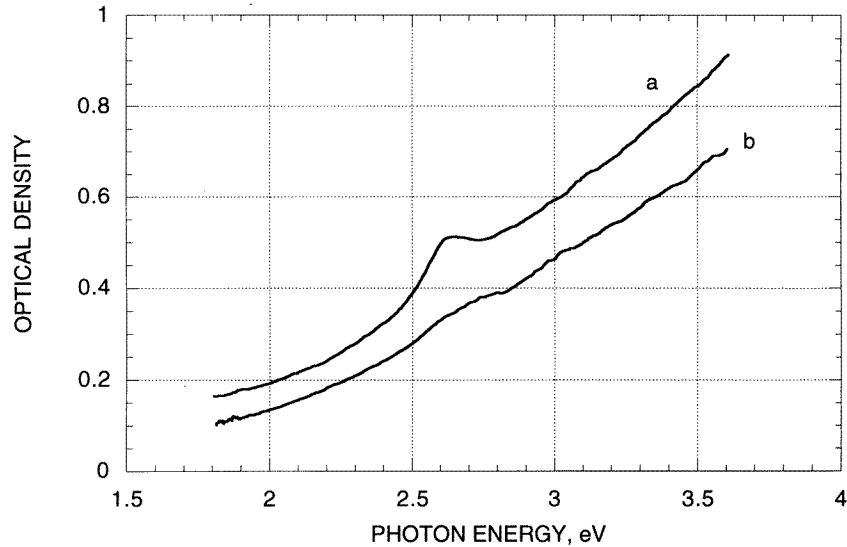
**Figure 5.** Optical absorption spectra of asb-CdSe for light polarized (a) along the channels and (b) perpendicular to the channels. The arrows show the energy position of the bulk CdSe absorption edge and the photon energy of the 632.8 nm line of the He-Ne laser used for the Raman spectra measurements.

CdSe filaments for  $E \parallel c$  (figure 5). The absence of the Raman bands in the  $aa$ -polarized spectrum is associated with the absence of the corresponding CdSe band in the absorption spectrum for  $E \perp c$ .

In this work, we have used sepiolite as a matrix for incorporation of a semiconducting material for the first time. The shape and structure of CdSe confined in the sepiolite channels have not been determined yet, but the observed absorption anisotropy (figure 6) can be considered as evidence for the existence of CdSe filaments or anisotropic clusters or chains inside sepiolite. A pronounced absorption band at 2.62 eV has been observed in the spectrum of sep-CdSe for  $E \parallel c$  (figure 6) (where  $c$  is the channel direction). The blue shift is about 0.9 eV compared with the bulk CdSe energy gap.

The size of the sepiolite channel is so small that we should expect some kind of molecular-like cluster or polymeric chain consisting of Cd and Se atoms inside channels. In this case, the absorption band at 2.62 eV should be attributed to the electron transition from the highest occupied molecular orbital to the lowest unoccupied molecular orbital. However, another point of view looks more reasonable. Probably, CdSe has been synthesized not in the original sepiolite channels but inside mesochannels. The mesochannels can be organized through the destruction of the original channel walls (figure 1(b)). This kind of mesochannel in the sepiolite has been observed by high-resolution TEM [9]. If we assume the formation of the CdSe quantum wires inside mesochannels and assign the 2.62 eV absorption band to the first intersubband transition, we can estimate the characteristic diameter of the cross section of the mesochannels. Using the same formula as for asb-CdSe, one can easily obtain a value for the filament diameter of about 3 nm. This is quite a reasonable value, but we need additional experiments to characterize sepiolite-confined CdSe correctly and to check alternative models.





**Figure 6.** Optical absorption spectra of sep-CdSe for light polarized (a) along the channels and (b) perpendicular to the channels.

#### 4. Conclusion

CdSe has been synthesized inside chrysotile asbestos and sepiolite channels. The TEM image shows filaments of 7–8 nm diameter inside asbestos channels. Resonance Raman spectra with the characteristic CdSe bands show that it is really CdSe. The significant anisotropy of the absorption and Raman spectra is a strong argument for stating that the spectra belong to the filaments. Within asbestos channels of several nanometres diameter, CdSe filaments can be considered as nanocylinders with the structure of bulk CdSe and the electron spectrum of the cylindrical quantum wires. The absorption band at 1.87 eV in the spectrum of asb-CdSe ( $E \parallel c$ ) can be attributed to transitions between size-quantized bands.

Sep-CdSe displays an absorption band at 2.62 eV ( $E \parallel c$ ) significantly shifted to higher energies compared with the bulk CdSe absorption edge. Two models for the sepiolite-confined CdSe are discussed: firstly, sepiolite-confined CdSe forms molecular-like clusters or one-dimensional chains in the crystalline channels; secondly CdSe filaments of diameters about 3 nm are stabilized in the mesochannels of the sepiolite.

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