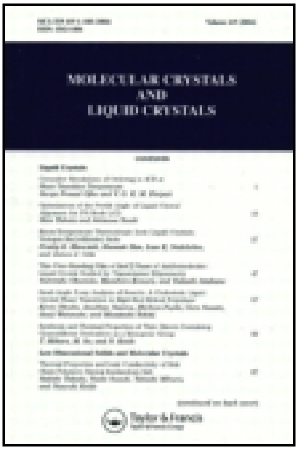

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# Optical and Related Properties of Some Natural Three and Lower Dimensional Semiconductor Systems

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# OPTICAL AND RELATED PROPERTIES OF SOME NATURAL THREE AND LOWER DIMENSIONAL SEMICONDUCTOR SYSTEMS

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Abstract New results concerning the optical absorption, photoconductivity, photoluminescence and photoluminescence-excitation spectra of $(CH_3NH_3)SnBr_3$ (3-D), $(C_6H_5CH_2CH_2NH_3)_2SnI_4$ (2-D), $Pt(en)_2$ $Pt(en)_2$ $Cl_2(ClO_4)_4$ (1-D), $Cd_xS_y(SPh)_z$ (0-D) and similar compounds (with:Pb, Ge instead of Sn; Pd, Ni instead of Pt; $Se_y$ instead of $S_y$) are reported. The spectra exhibit strong excitonic bands and in some cases impurity-bands in the UV-visible-near infrared spectral region.

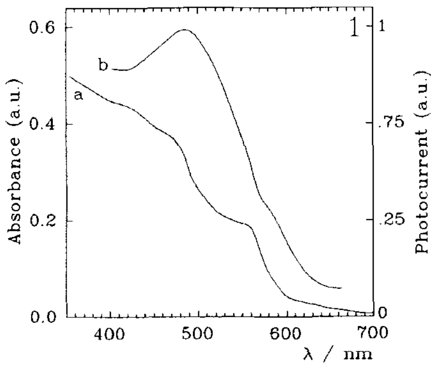
*Keywords: semiconductor, low dimensional, three dimensional, perovskite, quantum well, quantum wires, quantum dots, clusters*

## INTRODUCTION

During the last few years, rapid advances in materials technology have lead to the fabrication of novel electronic and optoelectronic devices based on low-dimensional(L-D) systems, i.e. quantum wells (2-D), quantum wires (1-D), and quantum dots (0-D). Artificial systems are fabricated by using several techniques, such as molecular beam epitaxy (for 2-D systems) or a combination of epitaxy, etching and lithography (for 1-D and 0-D systems) [1]. However, in addition to manmade structures, natural L-D systems (compound semiconductors) have long been known. Among the several different semiconductors studied in our institutes, the following natural systems were found by us to be more important for further investigations: 1) Compounds of the formula $(CH_3NH_3)MX_3$ (where M=Pb, Sn, Ge; X=Cl, Br, I) have a cubic perovskite structure and some of them are 3-D semiconductors [2-4]; 2) Compounds of the formulas $(CH_3NH_3)(C_nH_{2n+1}NH_3)_2M_2X_7$ and $(C_nH_{2n+1}NH_3)_2MX_4$ have layered perovskite structures and are 2-D semiconductors (natural quantum wells) [2-5]; 3) Compounds of the formula $M(L\text{-}L)_2M(L\text{-}L)_2X_2Y_4$ (where M=Pt, Pd, Ni; L-L=diamine; X=Cl, Br, I; $Y=ClO_4$, $BF_4$ etc) show 1-D semiconductor behaviour (natural quantum wires) [6,7]; and 4) small particles of CdS and similar compounds as well as clusters of the formula $Z_wM_xA_y(SPh)_z$ (where $Z=Me_4N$, $Me_3NH$ etc; M=Cd, Zn etc; A=S, Se) show 0-D semiconductor behaviour (natural quantum dots) [8,9]. All these natural systems are prepared by crystallization from solutions. In this paper new results concerning the optical absorption (OA), photoconductivity (PC), photoluminescence (PL) and photoluminescence excitation (PLE) spectra of these compounds are reported.

## $(CH_3NH_3)SnBr_3$ AND SIMILAR COMPOUNDS (3-D SYSTEMS)

The crystalline compound $(CH_3NH_3)SnBr_3$ and similar compounds (with Pb or Ge instead of Sn and Cl, I instead of Br) have been known for a long time (see refs [1-4] cited in ref [3] herein). $(CH_3NH_3)SnBr_3$ is crystallized in the cubic system, space group Pm3m with α=5.9053 Å. It has a cubic perovskite structure with a 3-D semiconductor behaviour [2,5]. It is red in colour. Fig.1 shows the OA spectrum of a thin film of $(CH_3NH_3)SnBr_3$ on quartz plate and the PC spectrum of a single crystal at room temperature. One can see that the OA spectrum shows a weak shoulder at ca 560 nm, which is attributed to excitons. There is no excitonic feature in the PC spectrum at room temperature. The excitonic peak is more pronounced in PL spectra as it is shown in Fig.2. Similar results were obtained from other similar compounds. Fig.2 shows also the PL spectra of $(CH_3NH_3)PbBr_3$ and $(CH_3NH_3)Pb_{0.4}Sn_{0.6}Br_3$. The OA and PL bands are broader than the corresponding 2-D systems (see next section). The weak shoulders, which occur at longer wavelengths, are due to impurities. They become more intense after exposure of the compounds to air and light. The behaviour of these systems is similar to that of conventional semiconductors, such as CdS and



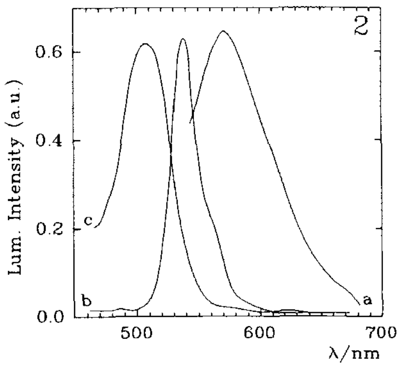


Fig.1. OA(a) and PC(b) spectra of $(CH_3NH_3)SnBr_3$ thin film (a) and single crystal (b) at room temperature.

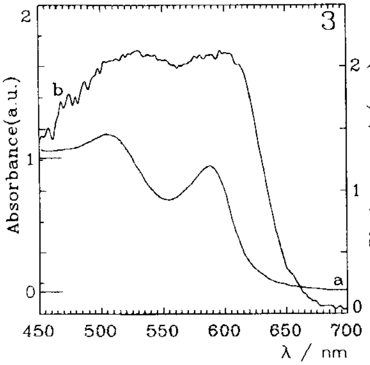
Fig.2. PL spectra of single crystals of $(CH_3NH_3)SnBr_3$ (a), $(CH_3NH_3)PbBr_3$ (b) and $(CH_3NH_3)Pb_{0.4}Sn_{0.6}Br_3$ (c) (excitation 454.5 nm).

GaAs [10]. Experiments concerning the variation of OA and PL features versus the temperature are in progress. It is expected that the values of excitonic binding energy will be smaller than that of the corresponding 2-D systems.

## $(C_6H_5CH_2CH_2NH_3)_2SnI_4$ AND SIMILAR COMPOUNDS (2-D SYSTEMS)

Crystals of $(C_6H_5CH_2CH_2NH_3)_2PbX_4$ (X=Cl, Br, I) and similar compounds with other alkylammonium or bis(alkylammonium) cations form natural multiquantum wells. In these compounds, the perovskite-like 2-D networks of $PbI_4$ correspond to the quantum wells, while the alkylammonium chains play the role of barriers (with small dielectric constant and much larger band-gap energy) and sandwich the wells. During the last years, structural, optical (linear and nonlinear) as well as other physical properties of this kind of materials have been reported (see [2,11-13] and refs therein). Recently, similar compounds of Sn have been prepared and characterized analytically and spectroscopically [2,3]. Some of them were prepared in single crystal form. Crystals of $(C_6H_5CH_2CH_2NH_3)_2SnI_4$ were obtained as rectangular platelets with a typical size of 5 x 1.5 x 0.5 $mm^3$. They are brown-golden in reflected light, or red-brown in transmitted light. The Br-analog is yellow in colour. $(C_6H_5CH_2CH_2NH_3)_2SnI_4$ is crystallized in the monoclinic system, space group C2/m, with a=32.64, b=6.117, c=6.164 Å, β=93.21 ° at room temperature [3,5]. It is isostructural with $(C_6H_5CH_2CH_2NH_3)_2PbI_4$ [12]. Fig. 3a shows the OA spectrum of a thin film of $(C_6H_5CH_2CH_2NH_3)_2SnI_4$ on quartz plate, observed at room temperature [3]. The main absorption peak at ca 590 nm is attributed to excitons. Fig. 3b shows the PC spectrum of a freshly prepared single crystal of $(C_6H_5CH_2CH_2NH_3)_2SnI_4$ at room temperature, with the electric field applied along the layer planes, so that the photocurrent flows perpendicular to the a-axis. The spectrum shows a maximum at 600 nm, namely, near the main absorption band. The blue shift of the absorption band may be due to the particulate structure of the film, as in the case of $PbI_4$-analogs (films and suspensions) [2]. Fig.4 shows the PL spectra of a single crystal of $(C_6H_5CH_2CH_2NH_3)_2SnI_4$ at room temperature (300 K) and at low temperature (ca 80 K). The room temperature spectrum shows a main peak at 625 nm, which is attributed to excitons. This peak is shifted to longer wavelengths as the temperature decreases. Also, the intensity of the peak depends on the temperature. Fig.5 shows the variation of the PL peak intensity versus inverse temperature. One can see that at low temperatures the intensity is almost constant, while at temperature values higher than that of ca 180 K the intensity decreases approximately as exp $(E_a/kT)$, with $E_a$=160-

190 meV. This means that the binding energy ($E_a$) of $(C_6H_5CH_2CH_2NH_3)_2SnI_4$ is lower than that of $(C_6H_5CH_2CH_2NH_3)_2PbI_4$ (>230 meV), but close to that of $(CH_3NH_3)(C_6H_5CH_2CH_2NH_3)_2Pb_2I_7$ (175 meV) [11]. The PL spectra show also a weak shoulder at ca 650 nm, which becomes more intense at low temperatures. This is attributed to impurities (shallow-trapped states [1,14]) resulting from photooxidation of the compound. Similar results have been obtained for $(C_6H_5CH_2CH_2NH_3)_2PbI_4$.



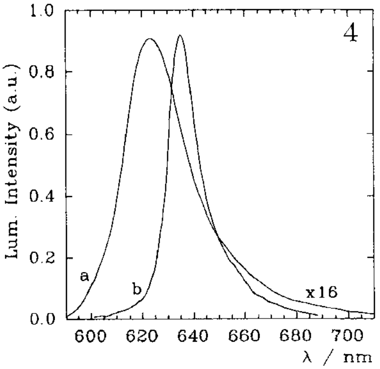
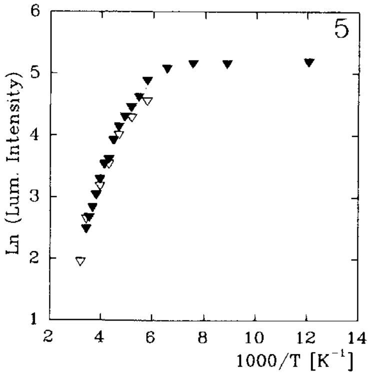


Fig.3. OA spectrum of a thin film of $(C_6H_5CH_2CH_2NH_3)_2SnI_4$ on quartz plate (a) and PC spectrum of a single crystal of $(C_6H_5CH_2CH_2NH_3)_2SnI_4$ at room temperature.

Fig.4. PL spectra of a single crystal of $(C_6H_5CH_2CH_2NH_3)_2SnI_4$ at room temperature(a) and at ca 80 K (b).



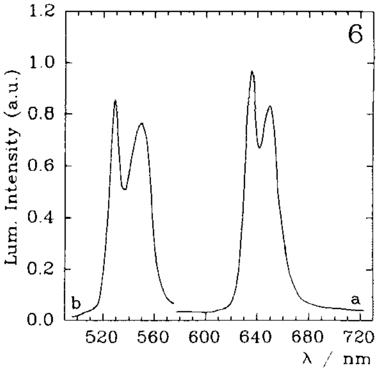
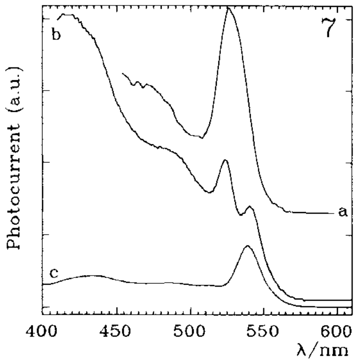


Fig. 5. PL intensity (on natural logarithmic scale), as a function of inverse temperature, of $(C_6H_5CH_2CH_2NH_3)_2SnI_4$ (data from two crystals).

Fig.6. PL spectra of $(C_6H_5CH_2CH_2NH_3)_2SnI_4$ (a) and $(C_6H_5CH_2CH_2NH_3)_2PbI_4$ (b) single crystals at ca 80 K after exposure to air and light for several days.

Fig.6 shows the PL spectra of $(C_6H_5CH_2CH_2NH_3)_2SnI_4$ and $(C_6H_5CH_2CH_2NH_3)_2PbI_4$ after exposure to the air and light for several days. The decrease of the intensity of the impurity-band versus the temperature is more rapid than that of Fig.5. This indicates that the corresponding binding energy [14] is larger than that of the excitonic band. Similar effects have been observed in the PC spectra. The PC bands due to impurities are well shown, even at room temperature. The results are more pronounced in the spectra of $(C_6H_5CH_2CH_2NH_3)_2PbI_4$. Fig.7 shows the room temperature PC spectrum of a freshly prepared single crystal of $(C_6H_5CH_2CH_2NH_3)_2PbI_4$ as well as spectra obtained after exposure to air and light. One can see that the excitonic peak at ca 525 nm (see also [11]) disappears and a new peak at ca 545 nm due to impurities appears after extensive exposure to air and light. Also, similar results were obtained after doping $(C_6H_5CH_2CH_2NH_3)_2PbI_4$ with $(C_6H_5CH_2CH_2NH_3)_2SnI_4$, as it is shown in Fig.8. The new peak, due to impurities occurs at ca 588 nm, while the corresponding OA band occurs at 512 nm. The OA spectrum of $(C_6H_5CH_2CH_2NH_3)_2SnBr_4$ and $(C_6H_5CH_2CH_2NH_3)_2GeI_4$ [4] show excitonic bands at 444 and 450 nm respectively.



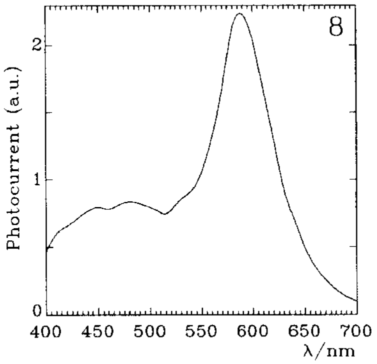


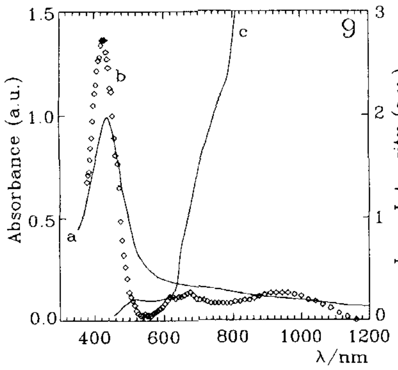
Fig.7. PC spectra of $(C_6H_5CH_2CH_2NH_3)_2PbI_4$ before (a), after exposure to air and light for several days (b) and after extensive exposure (for several weeks) (c).

Fig.8. PC spectrum of $(C_6H_5CH_2CH_2NH_3)_2PbI_4$ doped with $(C_6H_5CH_2CH_2NH_3)_2SnI_4$.

The PL spectra of this kind of materials do not show low frequency bands due to self-trapped excitons. The absence of resonance Raman bands at room temperature is due to the weak exciton-phonon interactions. Studies of PL spectra at low temperatures and of electroluminescence spectra are in progress.

## $Pt(en)_2Pt(en)_2Cl_2(ClO_4)_4$ AND SIMILAR COUMPOUNDS (1-D SYSTEMS)

$Pt(en)_2Pt(en)_2Cl_2(ClO_4)_4$ (where en=ethylenediamine) referred to hereafter as $Pt^{II}Pt^{IV}Cl_2$ is crystallized as red or greenish needle-like platelets. The crystals consist of $Pt^{II}(en)_2$ and $Pt^{IV}(en)_2$ units, which are stacked alternatively along the b-axis constructing a linear chain of Cl---$Pt^{II}$---Cl—$Pt^{IV}$— segments [15]. It behaves as 1-D semiconductor along the b-axis. Since the observation of 1-D semiconductor character of $Pt^{II}Pt^{IV}Cl_2$ [6], several research groups have studied linear and nonlinear optical properties of $Pt^{II}Pt^{IV}Cl_2$ and similar complexes of the type $M^{II}M^{IV}X_2$ (where M=Pt, Pd, Ni; X=Cl, Br, I) (see for example [6,7,15-20]). Moreover, properties of mixed-halide complexes, such as $Pt^{II}Pt^{IV}Cl_xBr_{2-x}$ [19] and some mixed-metal complexes, such as $M^{II}Pt^{IV}X_2$ [6,7,20], have been reported. Recently, we have prepared the mixed-metal of the type $M^{II}_x Pt^{II}_{1-x} Pt^{IV}X_2$ (X=Cl, Br), by cocrystallization of $M^{II}Pt^{IV}X_2$ and $Pt^{II}Pt^{IV}X_2$. Fig. 9a shows the OA spectrum of a thin deposit of $Pt^{II}Pt^{IV}Cl_2$ on quartz plate. There is a main peak at ca 438 nm, which is attributed to (charge transfer) excitons and some weak shoulders at longer wavelengths. The shoulders are more pronounced in the OA spectrum of Fig.9b obtained from the reflectance spectrum of a single crystal with polarization parallel to the chain axis by Kramers-Kronig transformation [7]. The weak peaks or shoulders, which are more intense at low temperatures are attributed to polarons, bipolarons etc.[16]. The PL spectrum of a single crystal (Fig.9c) shows an excitonic band at 520-540 nm, a shoulder at ca 740 nm, which corresponds to the polaronic (or impurities) absorption band. There is also a strong PL band at 1100 nm (it is not shown in Fig.9), which is attributed to self-trapped excitons [16]. The corresponding OA and PL bands of $Pd^{II}Pd^{IV}Cl_2$ and $Ni^{II}Ni^{IV}Cl_2$ occur at longer wavelengths than those of $Pt^{II}Pt^{IV}Cl_2$. Fig.10 shows the OA and PL spectra of $Pd^{II}_{0.2} Pt^{II}_{0.8} Pt^{IV}Cl_2$ and Fig.11 those of $Pd^{II}Pt^{IV}Cl_2$. The OA and PL bands occur at 386, 365 and 720, 666 nm, for $Pt^{II}_{0.2}Pt^{II}_{0.8}Pt^{IV}Cl_2$ and $Pd^{II}Pt^{IV}Cl_2$, respectively. Fig.12 shows the resonance Raman spectra of single crystals of $Pt^{II}Pt^{IV}Cl_2$, $Pd^{II}_{0.2}Pt^{II}_{0.8}Pt^{IV}Cl_2$ and $Pd^{II}Pt^{IV}Cl_2$. The corresponding lines occur at 311, 622, 935..., 318, 635, 955... and 323, 650, 970... $cm^{-1}$. Similar results have been obtained from Ni-analogs. From a small number of $M^{II}Pt^{IV}X_2$ examined until now, it is shown that the bands in the OA, PL and the lines in resonance Raman spectra occur in between those of the corresponding $M^{II}Pt^{IV}X_2$ and $Pt^{II}Pt^{IV}X_2$ complexes. By controlling the concentration of Pd or Ni in the crystals of $M^{II}_xPt_{1-x}^{II}Pt^{IV}X_2$ complexes, one can obtain the required OA bands in the spectral region 365-690 nm and the corresponding PL-bands in the region 666-1600 nm. The results are similar to those obtained from mixed-halide



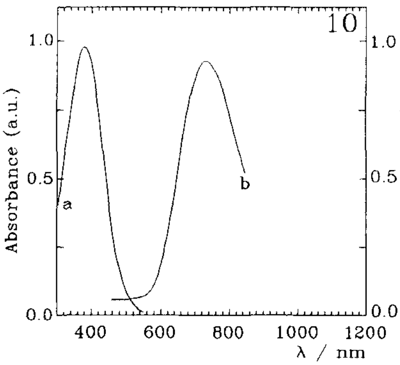
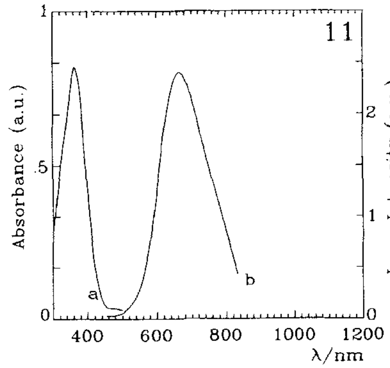


Fig.9. OA (a,b) and PL(c) spectra of a thin deposit (a) and of a single crystal (b,c) of $Pt^{II}Pt^{IV}Cl_2$ (red) (excitation 454.5 nm:Raman lines have been eliminated).

Fig.10. OA (a) and PL(b) spectra of a thin film (a) and a single crystal (b) of $Pd^{II}_{0.2}Pt^{IV}_{0.8}Pt^{IV}Cl_2$ (orange).



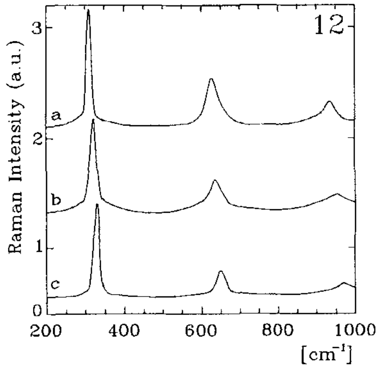


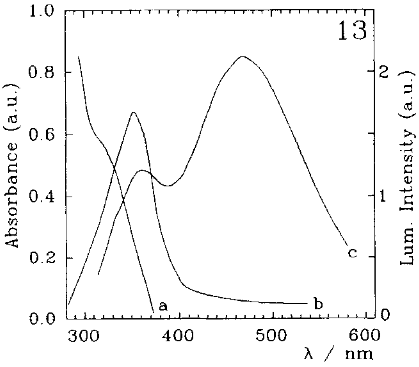
Fig.11. Same as Fig.10 but for $Pd^{II}Pt^{IV}Cl_2$ (yellow).

Fig.12. Resonance Raman spectra of $Pt^{II}Pt^{IV}Cl_2$ (a), $Pd^{II}_{0.2}Pt^{II}_{0.8}Pt^{IV}Cl_2$ (b) and $Pd^{II}Pt^{IV}Cl_2$(c) (excitation 454.5 nm).

complexes [19]. Studies of the OA, PL and resonance Raman spectra (with several different laser lines) of $M^{II}Pt^{II}Pt^{IV}X_2$ at room and lower temperatures are in progress.

## $Cd_xS_y(SPh)_z$ AND SIMILAR COMPOUNDS

Small particles of CdS and similar compounds with diameter smaller than the Bohr exciton diameter are 0-D systems. After the observation of quantum size effects in the OA, PL and resonance Raman spectra of CdS particles [8,21], several research groups studied linear and nonlinear optical properties in several semiconductors dispersed in liquids, polymers, glasses etc (see for example [9,22-24]). Also, small clusters with a $Cd_xS_y$ core have been prepared and studied in the last few years. Starting from the smaller cluster with formula $[Cd_{10}S_4(SPh)_{16}]^{4-}$ (diameter of 7 Å) [25] some clusters with larger core-size have been prepared by several methods. The preparation of $Cd_{10}S_{16}Ph_{12}$ (with a core diameter <10 Å) by heat treatment of $(Me_4N)_4Cd_{10}S_4(SPh)_{16}$ at ca 250 °C is reported in [26]. The OA spectrum of the cluster shows an excitonic shoulder at 335 nm, the corresponding PLE spectrum a band at 356 nm and the PL spectrum a broad band at ca 500 nm (deep-trap emission). From this cluster the preparation of another with formula $Cd_{32}S_{14}(SPh)_{36}(DMF)_4$ and core diameter of ca 15 Å is reported in [27]. The OA spectrum of this cluster shows an excitonic band at ca 358 nm. Also, a monodisperse cluster of the formula $[Cd_{20}S_{13}(SPh)_{22}]^{8-}$ with diameter of 10 Å is reported in [28]. The OA spectrum of this cluster exhibits a sharp excitonic band at 351 nm. Recently, we have prepared similar clusters of the type $Cd_xA_y(SPh)_z$ by electrolysis of $(Et_3NH)_4$ $Cd_{10}A_4(SPh)_{16}$ in acetonitrile (A is S or Se). The method is similar to that applied for preparation of cation-deficient complexes from the corresponding cation-rich complexes [29], or similar to that applied for preparation of $Cd_4(SPh)_8$ (single crystals, orthorhombic, space group $P2_12_12_1$) from $(Et_3NH)_2$ $Cd_4(SPh)_{10}$ [30]. The clusters $Cd_xA_y(SPh)_z$ were obtained as yellowish or yellow powders at the anode electrode or in the anodic branch of the electrolytic cell. From the peak positions of their OA spectra and the data of refs[26-28] concerning the size of clusters we found that the size of the clusters obtained by electrolytic method depends on the conditions of electrolysis, especially on the concentration. Diluted solutions of $(Et_3NH)_4$ $Cd_{10}S_4(SPh)_{16}$ in acetonitrile give a cluster $Cd_xS_y(SPh)_z$ with a core diameter (2R) larger than 7 Å and smaller than 10 Å. Fig.13 shows the OA, PLE and PL spectra of this cluster in tetrahydrofurane. The OA and PLE spectra are similar to those obtained by the heat-treatment method [26], but the PL spectrum, except the broad band at ca 470 nm (deep-trap emission), exhibits also an excitonic band at 360 nm (PLE at 352, OA at 320 nm). Concentrated solutions give clusters with $10<2R\leq15$ Å. Fig.14 shows the OA (355 nm), PLE (390 nm) and PL(410, 520 nm) bands. After heat-treatment the excitonic peak in PL spectra dissa-



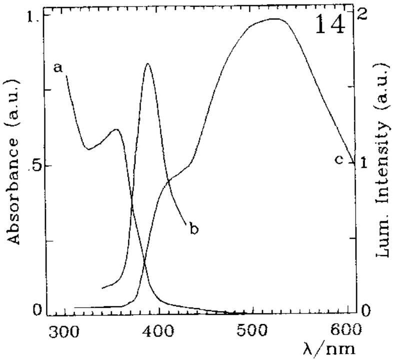


Fig. 13. OA(a), PLE(b, 580nm) and PL (c, 300 nm) spectra of $Cd_xS_y(SPh)_z$ with 7<2R<10Å.

Fig. 14. Same as in Fig.13, but for $Cd_xS_y(SPh)_z$ with $10 < 2R \leq 15$Å.

pears. The results are similar to those obtained from CdS particles [8,9]. The PL spectrum of 100 Å CdS particles, for example, shows an excitonic band at ca 470 nm and another band at ca 700 nm (self-trapped excitons). After heat-treatment the intensity of the excitonic band decreases and a new band appears at ca 560 nm. A red shift is observed in the spectral bands by increasing the cluster size. Similar results have been obtained from $Cd_xSe_y(SPh)_z$. Studies for clusters of other elements (Zn, Te etc) and other ligands ($CH_3C_6H_4S$ etc) are in progress and the results will be published elsewhere.

## REFERENCES

1. See for example C. Weisbuch and B. Vinter "Quantum Semiconductor Systems", Acad. Press., London (1991).
2. G. C. Papavassiliou, A. P. Patsis, D. J. Lagouvardos, and I. B. Koutselas, Synth. Metals 57, 3889 (1993).
3. G. C. Papavassiliou, J. B. Koutselas, and D. J. Lagouvardos, Z. Naturforsch. 48b, 1013 (1993).
4. G. C. Papavassiliou, A. Terzis, J. B. Koutselas, D. J. Lagouvardos, G. Papaioannou, to be published.
5. A. Terzis et al, to be published.
6. G. C. Papavassiliou, J. Phys. C: Sol. State Phys. 12, L297 (1979); G. C. Papavassiliou, T. Theophanides and R. Rapsomanikis, J. Raman Spectrosc. 8, 227 (1979); G. C. Papavassiliou, R. Rapsomanikis, S. Mourikis and C. S. Jacobsen, J. Chem. Soc., Faraday Trans. II, 78, 17 (1982).
7. G. C. Papavassiliou, in "Mixed Valency Systems" Edited by K. Prassides (Kluwer Acad. Publ. Netherlands), 343, 215 (1991) and refs. therein.
8. G. C. Papavassiliou, J. Sol. State Chem. 40, 330 (1981).
9. G. C. Papavassiliou, in "Nanostructural Materials: Synthesis, Properties and

Applications", edited by G. C. Hadjipanayis (Kluwer Acad. Publ., Netherlands), to be published (1994); and refs cited therein.

10. M. Cardona and G. Harkeke, Phys. Rev. 137A, 1465; C. Klick, ibid, 89, 274 (1953); D. Dutton, ibid., 112, 785 (1958); T. S. Moss and T. D. F. Hawkins, Infrared Physics 1, 111 (1961); D. C. Reynolds, Phys. Rev. 118, 478 (1960); R. J. Collins and J. J. Hopfield, ibid., 120, 840 (1960); B. Deveaud in "Optical Properties of Semiconductors", Ed. G. Markinez (Kluwer Acad. Publ. Netherlands), 228 E, 119 (1993).
11. T. Ishihara, X. Hong, J. Ding, and A. V. Nurmikko, Surface Sci., 267, 323 (1992); X. Hong, T. Ishihara, and A. V. Nurmikko, Sol. State Commun., 84, 657 (1992); Phys. Rev. B45, 6961 (1992); ICPS Proceedings, Beijing (1992).
12. J. Calabrese, N. L. Jones, R. L. Harlow, N. Herron, D. L. Thorn, and Y. Wang, J. Am. Chem. Soc., 113, 2328 (1991).
13. C.-q. Xu, S. Fukuta, H. Sakakura, T. Kondo, R. Ito, Y. Tokahashi, and K. Kumata, Sol. St. Commun. 77, 923 (1991).
14. G. T. Elnevoll and Y.-C. Chang, Phys. Rev. B40, 9683 (1989) and refs. therein.
15. S. C. Huckett, B. Scott, S. P. Love, R. J. Donahoe, C. J. Burns, Ed. Garcia, T. Frankcon and B. I. Swanson, Inorg. Chem. 32, 2137 (1993).
16. Y. Wada and M. Yamahita, Phys. Rev. B42 7398 (1990); Y. Tagawa and N. Suzuki, J. Phys. Soc. Jpn. 59 4074 (1990); K. Iwano and K. Nasu, ibid. 61, 1380 (1992); S. Abe, ibid 58, 62 (1989); R. J. Donohoe, L. A. Wore, C. A. Arrington, A. Bulou and B. I. Swanson, Phys. Rev. B 45, 13185 (1992); S. M. Weber-Milbrodt, J. T. Gammel, A. R. Bishop and E. Y. Loh, Jr, ibid 45, 6435 (1992).
17. M. Tanaka, S. Kurita, Y. Okada, T. Kajima and Y. Yamada, Chem. Phys. 96 343 (1985); R. J. H. Clark and D. J. Michael, J. Mol. Struct. 189, 173 (1988).
18. Y. Iwasa, E. Funatsu, T. Koda, M. Yamashita, H. Kobayashi and K. Kubodera, Mol. Cryst. Liq. Cryst. 217, 37 (1992); X. Sun, L. M. Li, R. T. Fu and K. Nasu, Synth. Metals 55-57, 3986 (1993).
19. K. Takahashi, H. Tanino, and T. Yao, Jpn. J. Appl. Phys. 26, L97 (1987); A. Saxena et al, Synth. Metals 54, 385 (1993); X.Z. Huang, A. Sexena, A. R. Bishop, L. A. Worl, S. P. Love and B. I. Swanson, Sol. St. Commun. 84, 457 (1989).
20. Y. Wada, T. Mitani, K. Toriumi, and M. Yamashita, J. Phys. Soc. Jpn. 58, 3013 (1989) and refs. cited therein.
21. C. Berry, Phys. Rev. 161, 848 (1967); R. Rossetti; S. Nakahera and L. E. Brus, J. Chem. Phys. 79, 1086 (1983).
22. L. Brus, J. Chem. Phys. 79, 5566 (1983); 80, 4403 (1984); 86, 2555 (1986); M. G. Bawend et al , ibid 96, 946 (1992); M. Grätzel, Ann. Chim. (Ital.) 77, 411 (1987).
23. Y. Wang and N. Herron, J. Phys. Chem. 91, 257 (1987); A. I. Ekimov and I. A. Kudrgarter, Bull. Russ. Acad. Sci., 56, 154 (1992).
24. S. Hayashi, H. Sanda, M. Agata and Y. Yamamoto, Phys. Rev. 40 , 5544 (1989).
25. G.S.H. Lee,K.Fisher, A.Vassado,J.Hanna and I.Dance, Inorg.Chem.32, 66(1993); I.G.Dance, A.Choy and M. L.Scudder, J.Am.Chem.Soc.106, 6285 (1984).
26. W. E. Farneth, N. Herron, and Y. Wang, Chem. Mater. 4, 916 (1992).
27. N. Herron, J. Calabrese, W. E. Farneth, and Y. Wang, Science, 259, 1426 (1993).
28. N. Herron, A. Suna and Y. Wang, J. Chem. Soc., Dalton Trans. 2329 (1992).
29. G. C. Papavassiliou, Z. Naturforsch., 37b, 825 (1982).
30. G. C. Papavassiliou and A. Terzis, to be published.