

# Optical Spectra and Structure of CdP<sub>4</sub> Nanoclusters Fabricated by Incorporation into Zeolite and Laser Ablation

O. A. Yeshchenko,\* I. M. Dmitruk, S. V. Koryakov, and M. P. Galak

Physics Department, National Taras Shevchenko Kyiv University,

2 Akademik Glushkov prosp., 03022 Kyiv, Ukraine

Received: July 6, 2005; In Final Form: August 25, 2005

CdP<sub>4</sub> nanoclusters were fabricated by incorporation into the pores of zeolite Na-X and by deposition of the clusters onto a quartz substrate using the laser ablation-evaporation technique. Absorption and photoluminescence (PL) spectra of CdP<sub>4</sub> nanoclusters in zeolite were measured at temperatures 4.2, 77, and 293 K. Both absorption and PL spectra consist of two blue-shifted bands. We performed DFT calculations to determine the most stable clusters configuration in the size region up to the size of the zeolite Na-X supercage. The bands observed in absorption and PL spectra were attributed to the emission of (CdP<sub>4</sub>)<sub>3</sub> and (CdP<sub>4</sub>)<sub>4</sub> clusters with binding energies of 3.78 and 4.37 eV per atom, respectively. The Raman spectrum of CdP<sub>4</sub> clusters in zeolite proved the fact of creation of (CdP<sub>4</sub>)<sub>3</sub> and (CdP<sub>4</sub>)<sub>4</sub> clusters in zeolite pores. The PL spectrum of CdP<sub>4</sub> clusters produced by laser ablation consists of a single band that was attributed to the emission of the (CdP<sub>4</sub>)<sub>4</sub> cluster.

## 1. Introduction

There are several methods for semiconductor nanoparticle fabrication, e.g., the fabrication of nanoparticles in solutions,<sup>1</sup> glasses,<sup>2</sup> or polymers.<sup>3</sup> However, it is not easy to control the size distribution of small nanoparticles with a countable number of atoms (so-called clusters) using these methods. The matrix method, based on the incorporation of materials into the 3D regular system of voids and channels of zeolite crystals, could be an alternative technique for the fabrication of semiconductor nanoclusters with a controllable size distribution.<sup>4,5</sup> Many works have been reported on the nanoclusters incorporated into zeolite pores: semiconductors,<sup>6–9</sup> metals,<sup>10,11</sup> and polymers.<sup>12,13</sup> The subnanometer and nanometer clusters are very interesting as they are intermediates between the molecules and the typical nanocrystals. Usually, the structure of nanoclusters is different from the structure of nanocrystals, which resembles the structure of bulk crystals.<sup>14</sup> As a rule, the calculation methods of the electronic states structure of nanocrystals that are based on the effective mass approximation are not applicable for clusters. Thus, nanoclusters are very interesting objects as their structure, electronic properties, and vibrational properties are quite different from those of the crystalline nanoparticles. Zeolites provide the opportunity to obtain extremely small clusters in the pores with diameters up to 15 Å. Zeolites are crystalline aluminosilicates with cavities whose diameters can vary in the range from 7 to 15 Å. The size of the cage depends on the kind of aluminosilicate framework, the ratio of Si/Al, the origin of ion-exchanged cations, which stabilize negative charge of framework, etc. Zeolite Na-X, which was used in the present work, has a Si/Al ratio equal to 1, *Fd3m* symmetry, and two types of cages: a sodalite cage (truncated octahedron with diameter 8 Å) and a supercage, which is formed by the connection of sodalites in diamondlike structure with a diameter of about 13 Å.<sup>15</sup> All cages are interconnected by shared small windows and

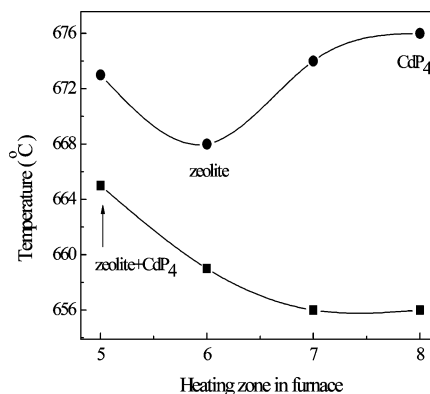
arranged regularly. Thus, the cages can be used for fabrication of small semiconductor nanoclusters.

Laser ablation (LA) is a well-known method for producing nanoclusters by ablating material from a solid target.<sup>16</sup> LA usually is performed in a vacuum or sometimes in inert gas, such as Ar, or more reactive gases, such as ammonia or nitrogen. Recently a new variation of LA has been reported whereby the target is immersed in a liquid medium and the laser beam is focused through the liquid onto the target surface.<sup>17</sup> The LA technique has been used to produce nanoclusters of semiconductors<sup>18</sup> and metals.<sup>19</sup>

Nanoclusters of II–V semiconductors have attracted not much attention so far. To the best of our knowledge, there are several works on Cd<sub>3</sub>P<sub>2</sub> nanoclusters fabricated by wet chemistry methods<sup>20</sup> and by thermolysis<sup>21</sup> and alcoholysis of organometallic species.<sup>22</sup> As well, in our recent work<sup>23</sup> we have reported the fabrication and study of the optical properties of the nanoclusters of another II–V semiconductor (ZnP<sub>2</sub>) incorporated into the zeolite Na-X matrix. The present paper is the first study of the nanoclusters of another II–V semiconductor: cadmium tetraphosphide (CdP<sub>4</sub>). Wet chemistry methods seem to us not to be suitable for the production of small II–V nanoclusters due to their high reactivity in water. It is hard to expect their high stability in glass melt as well. Thus, the incorporation into zeolite cages and the production by pulsed laser ablation seem to us to be the most suitable methods for II–V semiconductor nanoclusters fabrication.

Quantum confinement of charge carriers in nanoclusters leads to new effects in their optical properties. Those are the blue-shift of exciton spectral lines originating from the increase of the kinetic energy of charge carriers and the increase of the oscillator strength per unit volume.<sup>24</sup> These effects are quite remarkable when the radius of the nanoparticle is comparable with the Bohr radius of exciton in bulk crystal. Incorporation into zeolite pores and laser ablation are quite promising methods for the fabrication of small nanoclusters where the quantum confinement plays an important role.

\* Author to whom correspondence should be sent: O. A. Yeshchenko. Tel.: +380-44-5264587; Fax: +380-44-5264036; e-mail: yes@univ.kiev.ua.



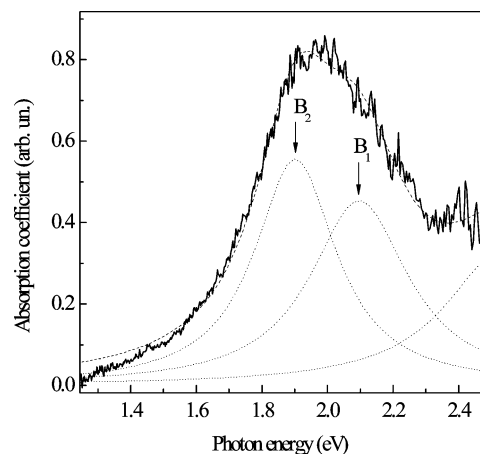
**Figure 1.** Temperature gradients used at the first stage (●) and at the second stage (■) of the fabrication of CdP<sub>4</sub> clusters in zeolite Na-X.

Bulk CdP<sub>4</sub> crystal is the direct-gap semiconductor<sup>25</sup> with an energy gap of 0.908 eV. The lattice symmetry is characterized by the space symmetry group  $C_{2h}^5$  (monoclinic syngony). Because the bulk crystal has a rather narrow energy gap, the blue-shifted spectral lines of CdP<sub>4</sub> nanoclusters are expected to be in the visible or near-IR spectral region.

## 2. Technology of Fabrication of CdP<sub>4</sub> Nanoclusters. Experimental Procedures

The high-purity CdP<sub>4</sub> bulk crystals and synthetic zeolite of Na-X type were used for the fabrication of CdP<sub>4</sub> nanoclusters. The framework of zeolite Na-X consists of sodalite cages and supercages with inner diameters of 8 and 13 Å, respectively. CdP<sub>4</sub> nanoclusters are too large to be incorporated into a small sodalite cage due to the existence of many Na cations. Therefore, it is natural to assume that only the supercages can be hosts for the nanoclusters. Zeolite and CdP<sub>4</sub> crystals were dehydrated in a quartz-sealed ampule in a vacuum of about  $2 \times 10^{-5}$  mmHg for 1 h at 400 °C. We used a 100-mm length ampule for space separation of the semiconductor source and zeolite. The fabrication of samples was carried out in two stages. At the first stage (see Figure 1), CdP<sub>4</sub> was incorporated into the zeolite matrix through the vapor phase at 676 °C in the source region and at 668 °C in the zeolite region for 100 h. At the second stage, the inverted temperature gradient was applied: 656 °C in the source region and 665 °C in the zeolite region. The duration of the second stage was 40 h. The cooling of the ampule was carried out gradually with the inverted temperature gradient mentioned above. The inverted temperature gradient was aimed to clean the surface of the zeolite crystals from CdP<sub>4</sub> film and large particles that, probably, can appear on the zeolite surface. The stability of the structure of the lattice of zeolite single crystals was controlled by the XRD method. The control showed that the zeolite lattice structure was stable at the temperatures mentioned above; i.e., the clusters were incorporated into the single-crystal zeolite matrix. At the end of the incorporation process, no free cadmium or phosphorus was observed in the ampule.

The optical spectra were measured from the samples placed both in a vacuum in a quartz ampule and in air. A tungsten-halogen incandescent lamp was used as a light source for the diffuse reflection measurements. An Ar<sup>+</sup> laser with wavelength 514.5 nm was used in luminescence and Raman experiments. The absorption spectra of the nanoclusters were obtained from the diffuse reflection spectra by conversion with the Kubelka–Munk function  $K(\hbar\omega) = [1 - R(\hbar\omega)]^2/2R(\hbar\omega)$ , where  $R(\hbar\omega)$  is the diffuse reflectance normalized by unity at the region of no absorption.



**Figure 2.** Absorption spectrum of CdP<sub>4</sub> clusters in zeolite Na-X at the temperature 77 K.

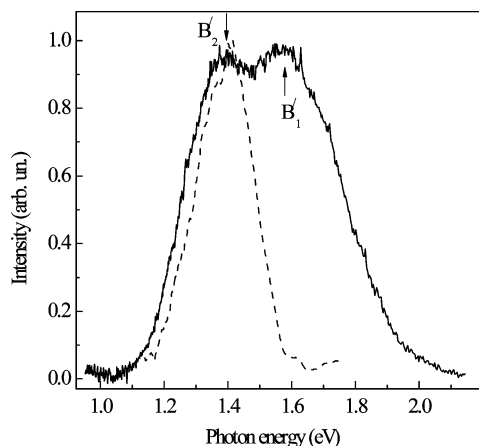
For ablation, the pulsed Cu laser ( $\lambda = 578.2$  nm) was used. The pulse intensity of the focused laser beam was about 1.5 MW/cm<sup>2</sup>; the pulse duration was 20 ns at a repetition rate of 10 kHz. The beam was focused on the surface of the target to a spot-size diameter of approximately 0.5 mm. During the ablation, the target (bulk CdP<sub>4</sub> crystal of area 9 mm<sup>2</sup>) was dipped into the liquid nitrogen. The nanoclusters of CdP<sub>4</sub> produced by ablation were deposited on a quartz plate that was positioned at a distance of about 0.2 mm from the surface of the target crystal. The run time of ablation was 20 min. The photoluminescence spectrum was measured from the deposited film excited by an Ar<sup>+</sup> laser ( $\lambda = 514.5$  nm).

## 3. Structure and Optical Properties of CdP<sub>4</sub> Nanoclusters

Diffuse reflection (DR) and photoluminescence (PL) spectra of the CdP<sub>4</sub> nanoclusters incorporated into the pores of zeolite Na-X were measured at room (293 K), liquid nitrogen (77 K), and liquid helium (4.2 K) temperatures. Then, the DR spectrum was converted to absorption using the Kubelka–Munk method described above. Within the accuracy of determination of the spectral positions of the bands, we did not observe a noticeable change of either absorption or PL spectra with temperature. Optical spectra of the clusters were the same both in a vacuum in a quartz ampule and exposed to the normal atmospheric condition. This is evidence of the stability of CdP<sub>4</sub> clusters in the pores of zeolite placed in air. The absorption spectrum obtained by the Kubelka–Munk method is presented in Figure 2. The spectrum demonstrates a two-band structure. The spectral positions of the respective bands assigned as B<sub>1</sub> and B<sub>2</sub> are presented in Table 1. Both bands are blue-shifted (see Table 1); the shift values are calculated using the energy gap of the bulk CdP<sub>4</sub> crystal (0.908 eV). Note that the blue-shift of the high-energy absorption band for CdP<sub>4</sub> clusters in Na-X zeolite is considerably larger than respective one for ZnP<sub>2</sub> clusters in the same zeolite:<sup>23</sup> 1.353 eV for CdP<sub>4</sub> and 0.808 eV for ZnP<sub>2</sub>. The observed blue-shift allows us to attribute these bands to the absorption in the first electronic excited state of the CdP<sub>4</sub> nanoclusters incorporated into supercages of the zeolite. The photoluminescence spectrum of CdP<sub>4</sub> clusters in zeolite (Figure 3) shows the same structure as that of the absorption; i.e., the PL spectrum consists of the corresponding two B'<sub>1</sub> and B'<sub>2</sub> bands. Their spectral positions are presented in Table 1. PL bands of nanoclusters are blue-shifted as well. The observed blue-shift of the absorption and luminescence bands is the result of the quantum confinement of electrons and holes in CdP<sub>4</sub> nanoclusters.

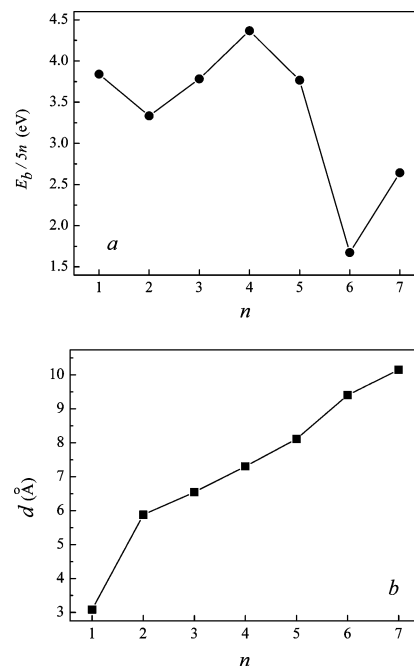
**TABLE 1: Spectral Characteristics of CdP<sub>4</sub> Clusters in Zeolite Na-X and Clusters Produced by Laser Ablation**

spectral position (eV)			blue-shift of absorption band (eV)	stokes shift (eV)	
absorption	zeolite Na-X	ablation		zeolite Na-X	ablation
2.261 (B <sub>1</sub> )	1.577 (B' <sub>1</sub> )		1.353 (B <sub>1</sub> )	0.684 (B <sub>1</sub> - B' <sub>1</sub> )	
1.902 (B <sub>2</sub> )	1.397 (B' <sub>2</sub> )	1.407 (B'' <sub>2</sub> )	0.994 (B <sub>2</sub> )	0.505 (B <sub>2</sub> - B' <sub>2</sub> )	0.495 (B <sub>2</sub> - B'' <sub>2</sub> )

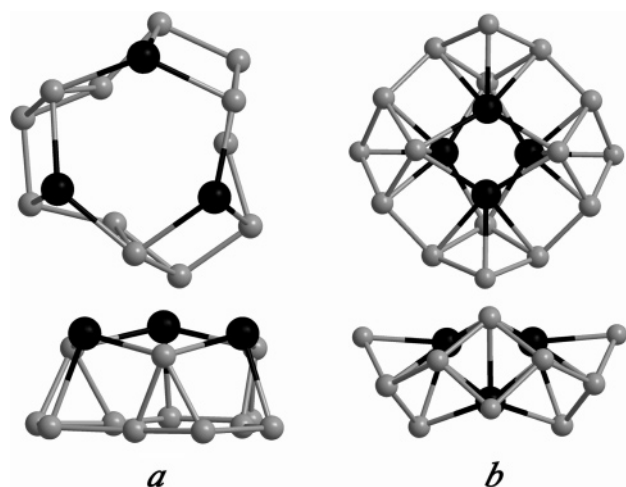
**Figure 3.** Photoluminescence spectrum of CdP<sub>4</sub> clusters in zeolite Na-X (solid curve) and PL spectrum of CdP<sub>4</sub> clusters fabricated by laser ablation (dashed curve) at the temperature 77 K.

Besides the clusters in zeolite pores, we fabricated the CdP<sub>4</sub> nanoclusters by the pulsed laser ablation technique described above. The obtained PL spectrum of CdP<sub>4</sub> clusters is shown in Figure 3. The spectrum consists of a single band. One can see that the spectral position of the maximum of the band, marked as B''<sub>2</sub>, coincides with the position of B'<sub>2</sub> band of the luminescence spectrum of CdP<sub>4</sub> clusters in zeolite (Taking into account rather large half-widths of B'<sub>2</sub> and B''<sub>2</sub> bands, the small (0.01 eV) discrepancy in their maxima positions is negligible.). This fact and the proximity of the values of the half-widths of the B''<sub>2</sub> and the B'<sub>2</sub> bands (0.183 and 0.178 eV, correspondingly) allow us to assume the same origin of these PL bands.

However, what kind of CdP<sub>4</sub> clusters cause an appearance of the bands in optical spectra? It is often observed that nanoclusters with a certain number of atoms are characterized by increased stability (ultrastable nanoclusters) and are more abundant in the sample. This effect is well-known for the nanoclusters of different types, e.g. for C,<sup>26</sup> Ar,<sup>27</sup> Na,<sup>27</sup> and nanoclusters of II–VI semiconductors.<sup>28</sup> Our calculations<sup>23</sup> have shown that such stable nanoclusters exist for ZnP<sub>2</sub>, that is semiconductor of the II–V type as well as CdP<sub>4</sub>. Those are (ZnP<sub>2</sub>)<sub>6</sub> and (ZnP<sub>2</sub>)<sub>8</sub> with binding energies 1.72 and 2.14 eV per atom, respectively. Thus, it would be natural to assume that, similar to ZnP<sub>2</sub>, the respective stable (CdP<sub>4</sub>)<sub>n</sub> nanoclusters exist for CdP<sub>4</sub> as well. We performed the calculations, aiming to find such stable (CdP<sub>4</sub>)<sub>n</sub> clusters. We considered the stoichiometric clusters only, because no free cadmium nor phosphorus was observed in the ampule, as mentioned above. Initially, we performed the geometry optimization of the structure of clusters by the molecular mechanics MM+ method. Then, we performed the ab initio calculation (by STO-3G basis set) of the ground-state energy of the clusters with optimized structure. The results are presented in Figures 4 and 5. One can see that the (CdP<sub>4</sub>)<sub>4</sub> cluster is the most stable, and clusters with  $n = 1, 3, 5$  have the close values of the binding energy; namely, (CdP<sub>4</sub>)<sub>4</sub> has the binding energy of 4.37 eV per atom, (CdP<sub>4</sub>)<sub>1</sub> = 3.84 eV, (CdP<sub>4</sub>)<sub>3</sub> = 3.78 eV, and (CdP<sub>4</sub>)<sub>5</sub> = 3.77 eV. The clusters with  $n = 2, 6,$

**Figure 4.** Results of the ab initio calculations of (CdP<sub>4</sub>)<sub>n</sub> cluster binding energy per atom (a) and maximum diameter of the cluster (b) versus  $n$ .

and 7 have a considerably lower binding energy. Thus, the (CdP<sub>4</sub>)<sub>n</sub> clusters are bound considerably stronger than the respective (ZnP<sub>2</sub>)<sub>n</sub> clusters. It is natural to assume that some other stable (CdP<sub>4</sub>)<sub>n</sub> clusters with  $n > 7$  exist as well. However, our estimation of the diameter of the largest (CdP<sub>4</sub>)<sub>n</sub> cluster that might be placed in the zeolite Na-X supercage is 9.28 Å. Our estimations take into account the van der Waals radii of Cd (1.940 Å) and P (1.784 Å). Therefore, the clusters with  $n \geq 6$  cannot be incorporated into supercages of the Na-X zeolite. Here and everywhere in the article, the maximum diameter of the cluster means the distance between the centers of the outermost atoms of the cluster. Because the (CdP<sub>4</sub>)<sub>4</sub> cluster is the most stable, it is quite reasonable to assume that this cluster is the most abundant. Correspondingly, the (CdP<sub>4</sub>)<sub>4</sub> cluster would be formed in prevalent quantities at the ablation. An effect of the prevalence of the most stable nanoclusters in mass spectra is well-known for II–VI semiconductors.<sup>28</sup> Meanwhile, laser ablation is the method for the production of analyzed particles in mass spectrometry. It is natural that other CdP<sub>4</sub> nanoclusters, besides (CdP<sub>4</sub>)<sub>4</sub>, would be formed at the ablation as well, but probably, their quantity is quite small compared to the quantity of (CdP<sub>4</sub>)<sub>4</sub> clusters. Therefore, these less abundant clusters would not give a considerable contribution to the PL spectrum. Thus, it is natural to assume that the B''<sub>2</sub> band of the PL spectrum of clusters fabricated at the ablation originates from the (CdP<sub>4</sub>)<sub>4</sub> cluster. As we have noted above, the B'<sub>2</sub> band of the PL spectrum of clusters incorporated into zeolite has the same origin as the B''<sub>2</sub> band. Therefore, the low-energy luminescence B'<sub>2</sub> band and the respective absorption B<sub>2</sub> band originate from the most stable (CdP<sub>4</sub>)<sub>4</sub> cluster. And what is the origin of the high-

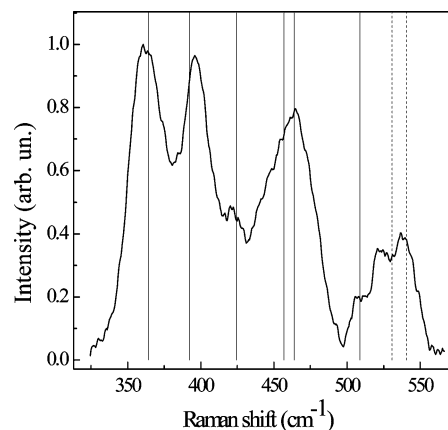


**Figure 5.** Calculated structure of  $(\text{CdP}_4)_n$  clusters: (a) structure of the  $(\text{CdP}_4)_3$  cluster, and (b) structure of the  $(\text{CdP}_4)_4$  cluster; Cd atoms = black balls, P atoms = gray balls.

energy absorption  $B_1$  and the respective luminescence  $B'_1$  bands of clusters in zeolite? Because these bands are characterized by higher energies, they would originate from the clusters smaller than  $(\text{CdP}_4)_4$  one. Those can be  $(\text{CdP}_4)_1$  and  $(\text{CdP}_4)_3$ , which are characterized by close values of binding energy.

To clarify the problem of the origin of the  $B_1$  and  $B'_1$  bands, we performed the Raman study of the clusters in zeolite. The measured Raman spectrum is shown in Figure 6. To answer the question of what kind of clusters are formed in zeolite pores, we performed a semiempirical calculation (by the AM1 method) of the vibrational spectrum of the  $\text{CdP}_4$  clusters that may fit into the zeolite supercage. Calculations showed that the vibrational spectra of only  $(\text{CdP}_4)_4$  and  $(\text{CdP}_4)_3$  clusters agree in satisfactory way with the experimental Raman spectrum. Therefore, the Raman spectrum shows that  $(\text{CdP}_4)_4$  and  $(\text{CdP}_4)_3$  clusters are formed in zeolite pores. Therefore, we can conclude that  $B_1$  and  $B'_1$  bands originate from the absorption and emission transitions, respectively, in the  $(\text{CdP}_4)_3$  cluster. The presence of the  $B'_1$  band originating from the  $(\text{CdP}_4)_3$  cluster in the PL spectrum of clusters in zeolite is due to the difficulty of penetration of the  $\text{CdP}_4$  substance into most inner areas of zeolite crystals. Therefore, in these areas the smaller clusters with lower binding energy would be formed. Thus,  $B_1-B'_1$  and  $B_2-B'_2$  ( $B'_2$ ) bands can be attributed to originate from the stable  $(\text{CdP}_4)_3$  and  $(\text{CdP}_4)_4$  nanoclusters mentioned above. The calculated structure of these clusters is presented in Figure 5. One can see from the figure that due to the difference of the covalent radii of Cd and P atoms, the  $(\text{CdP}_4)_3$  and  $(\text{CdP}_4)_4$  clusters have beltlike structures.

One can see from the Table 1 that the luminescence bands have the Stokes shift from the absorption bands. The values of this shift are large enough: 0.684 eV for the  $B'_1$  band and 0.505 eV for the  $B'_2$  band. These values are considerably larger than those for  $\text{ZnP}_2$  nanoclusters in the same Na-X zeolite (0.078–0.135 eV).<sup>23</sup> Stokes shift is well-known both in the molecular spectroscopy and in the spectroscopy of nanoclusters. This kind of Stokes shift (so-called Franck–Condon shift) is due to the vibrational relaxation of the excited molecule or nanoparticle to the ground state. The theory of the Franck–Condon shift in nanoclusters was developed by Franceschetti and Pantelides,<sup>29</sup> where the first-principle calculations of excited-state relaxations in nanoclusters were performed. They showed that, for small nanoclusters, the Stokes shift is the Franck–Condon shift, which is the result of the vibrational relaxation of the nanoparticle in the excited electronic state. The consider-



**Figure 6.** Raman spectrum of  $\text{CdP}_4$  clusters in zeolite Na-X at the temperature 293 K. Solid lines mark the calculated vibrational frequencies of the  $(\text{CdP}_4)_4$  cluster and dashed lines mark the respective frequencies of the  $(\text{CdP}_4)_3$  cluster.

able values of the Stokes shift in  $(\text{CdP}_4)_n$  clusters show the substantial role of vibrational relaxation in excited nanoparticles.

#### 4. Conclusions

In conclusion, subnanometer  $(\text{CdP}_4)_n$  clusters have been prepared both by incorporation into zeolite Na-X pores from the vapor phase and by laser ablation in liquid nitrogen media. Absorption and photoluminescence spectra of clusters in zeolite and PL spectrum of clusters obtained by the LA method demonstrate a quite-large blue-shift. The semiempirical search of the stable structures and the ab initio calculations of the binding energy of  $(\text{CdP}_4)_n$  clusters have been performed up to  $n = 7$ . The results of spectroscopic study and calculations have allowed us to assume the creation of  $(\text{CdP}_4)_n$  clusters with  $n = 3, 4$  in zeolite pores and clusters with  $n = 4$  in LA experiments. The Raman spectrum of the clusters in zeolite has proved the creation of  $(\text{CdP}_4)_3$  and  $(\text{CdP}_4)_4$  clusters in zeolite pores.

#### References and Notes

- (1) Kumbhojkar, N.; Nikesh, V. V.; Kshirsagar, A.; Nahamuni, S. *J. Appl. Phys.* **2000**, *88*, 6260.
- (2) Armelao, L.; Bertocello, R.; Cattaruzza, E.; Gialanella, S.; Gross, S.; Mattei, G.; Mazzoldi, P.; Tondello, E. *J. Appl. Chem.* **2002**, *12*, 2401.
- (3) Motte, L.; Pileni, M. P. *Appl. Surf. Sci.* **2000**, *164*, 60.
- (4) Stucky, G. D.; Mac Dougall, J. E. *Science* **1990**, *247*, 669.
- (5) Bruhwiler, D.; Calzaferri, G. *Microporous Mesoporous Mater.* **2004**, *72*, 1.
- (6) Wang, Y.; Herron, N. *J. Phys. Chem.* **1988**, *92*, 4988.
- (7) Herron, N.; Wang, Y.; Eddy, M. M.; Stucky, G. D.; Cox, D. E.; Moller, K.; Bein, T. *J. Am. Chem. Soc.* **1989**, *111*, 530.
- (8) Tang, Z. K.; Nozue, Y.; Goto, T. *J. Phys. Soc. Jpn.* **1992**, *61*, 2943.
- (9) Tanaka, K.; Komatsu, Y.; Choo C.-K. *J. Phys. Chem. B* **2005**, *109*, 736.
- (10) Nozue, Y.; Kodaira, T.; Goto, T. *Phys. Rev. Lett.* **1992**, *68*, 3789.
- (11) Ikemoto, Y.; Nakano, T.; Kuno, M.; Nozue, Y. *Physica B* **2000**, *281*, 282, 691.
- (12) Cox, S. D.; Gier, T. E.; Stucky, G. D.; Bierlein, J. *J. Am. Chem. Soc.* **1988**, *110*, 2986.
- (13) Wu, C.-G.; Bein, T. *Science* **1994**, *266*, 1013.
- (14) Martin, T. P. *Phys. Rep.* **1996**, *273*, 199.
- (15) Corma, A. *Chem. Rev.* **1995**, *95*, 559.
- (16) Shirk, M. D.; Molian, P. A. *J. Laser Appl.* **1998**, *10*, 18.
- (17) Simakin, A. V.; Shafeev, G. A.; Loubnin, E. N. *Appl. Surf. Sci.* **2000**, *154*, 405.
- (18) Hartanto, A. B.; Ning, X.; Nakata, Y.; Okada, T.; *Appl. Phys. A: Mater. Sci. Process* **2004**, *78*, 299.



- (19) Dolgaev, S. I.; Simakin, A. V.; Voronov, V. V.; Shafeev, G. A. *Appl. Surf. Sci.* **2002**, *186*, 546.
- (20) Zhao, X.-G.; Shi, J.-L.; Hu, B.; Zhang, L.-X.; Hua, Z.-L. *J. Mater. Chem.* **2003**, *13*, 399.
- (21) Green, M.; O'Brien, P. *Adv. Mater.* **1998**, *10*, 527.
- (22) Green, M.; O'Brien, P. *J. Mater. Chem.* **1999**, *9*, 243.
- (23) Yeshchenko, O. A.; Dmitruk, I. M.; Koryakov, S. V.; Pundyk, I. P.; Barnakov, Y. A. *Solid State Commun.* **2005**, *133*, 109.
- (24) Brus, L. E. *J. Phys. Chem.* **1986**, *90*, 2555.
- (25) Radautsan, S. I.; Syrbu, N. N.; Teslevan, V. E.; Chumak, J. V. *Phys. Status Solidi B* **1973**, *60*, 415.
- (26) Kroto, H. W.; Heath, J. R.; O'Brien, S. C.; Curl, R. F.; Smalley, R. E. *Nature* **1985**, *318*, 162.
- (27) Connerade, J.-P.; Solov'ov, A. V.; Greiner, W. *Europhys. News* **2002**, *33* (6), 200.
- (28) Kasuya, A.; Sivamohan, R.; Barnakov, Y. A.; Dmitruk, I. M.; Nirasawa, T.; Romanyuk, V. R.; Kumar, V.; Mamykin, S. V.; Tohji, K.; Jeyadevan, B.; Shinoda, K.; Kudo, T.; Terasaki, O.; Liu, Z.; Belosludov, R. V.; Sundararajan, V.; Kawazoe, Y. *Nat. Mater.* **2004**, *3*, 99.
- (29) Franceschetti, A.; Pantelides, S. T. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2003**, *68*, 033313.