

Dielectric Function of (CdSe)₁₃ Clusters

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We investigate theoretically the atomic and electronic structures of (CdSe)₁₃ cluster which is of the smallest magic number size among (CdSe)_n found experimentally recently. Using the first-principles approach based on the local density approximation in the density functional theory, we calculate the dielectric function for two cluster geometries of (CdSe)₁₃ and compare the results with the changes in the optical absorption spectra under the illumination.

Key words: optical absorption spectra, dielectric response function, density functional theory, first principles

1. INTRODUCTION

Quite recently, (CdSe)_n clusters have been synthesized and characterized by the optical and time-of-flight (TOF) mass measurements by Barnakov *et al.*[1,2]. The TOF mass spectra of positive ions show that (CdSe)₁₃ is an abundant magic number cluster. Kumar *et al.* [3] have determined the most stable geometry of the clusters by means of the standard *ab initio* pseudopotential approach based on the local density approximation (LDA) in density functional theory. The magic (CdSe)₁₃ cluster has an endohedral cage structure composed of twelve Se ions at the surface of an icosahedral cage, one Se ion at the center and thirteen Cd ions at slightly inner than the cage surface. The main interest of these clusters lies in their specific behavior in the optical response.

In the present paper, we calculate, for the first time, the dielectric function of (CdSe)₁₃ and compare the results with the optical absorption spectra measured by Kasuya *et al.* [1]. In addition to the most stable cage structure, we consider another structure of (CdSe)₁₃ which can be obtained by cutting the bulk wurtzite and by optimizing their geometrical structures. Throughout this paper, we use *ab initio* methods within the LDA in density functional theory.

2. EXPERIMENT

(CdSe)_n clusters was created by following sequence :

- i . Solution of CdNTA and Na₂SeSO₃ was mingled with decylamine (CH₃(CH₂)₉NH₂) as surfactant. (Cd²⁺ and Se²⁻ was created in solution)
- ii . Toluene was added to the above mixture at temperature of 45°C. (The clusters grew up in nearby boundary face of toluene and solution.)
- iii. The resultant greenish yellow solution of toluene

was concentrated and aged for a week.

The optical absorption spectra of (CdSe)_n were measured in toluene after illumination by xenon lamp combined with a monochromater to observe photo illumination effects.

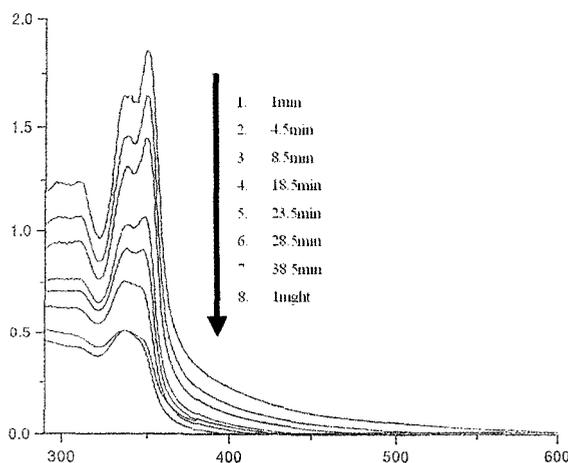


Fig. 1 Optical absorption spectra measured for the (CdSe)₁₃ sample in toluene. The abscissa is the light wavelength in units of nm and the ordinate is in arbitrary units. The eight curves (from up to bottom) correspond, respectively, to the observations after 1 min, 4.5 min, 8.5 min, 18.5 min, 23.5 min, 28.5 min, 38.5 min and 1 night light illumination of tungsten lamp after dissolving (CdSe)₁₃ in the solvent.

Figure 1 shows the optical absorption spectra of (CdSe)₁₃ clusters. The clusters also have the surfactant molecules, decylamine. It exhibits sharp peaks around 340-350nm. The eight curves in this figure represent the change of the observed spectra with the illumination times given in the figure. The uppermost curve is the

observation after 1 min of light illumination, while the lowermost curve is the observation of the clusters after its leaving for one night with the previous light illumination of the clusters by 38.5 min. As it is seen from the comparison of lowermost and its previous curves, the difference is negligible. It says that suspension of clusters is rather stable with a time, however its external perturbation by light source results in the changes of peak intensities and small blue-shift.

In order to investigate the $(\text{CdSe})_n$ clusters having time dependence, we have repeated calculations with the same cutoff energies for three different supercell sizes: $a = 16 \text{ \AA}$, 20 \AA and 24 \AA .

3. FIRST PRINCIPLE CALCULATION

We first performed structural optimization by means of the ultrasoft-pseudopotential program (VASP) [4] to obtain the locally stable wurtzite structure as well as the most stable endohedral cage structure that has already been done in Refs. [1-3]. The geometries of the resulting optimized $(\text{CdSe})_{13}$ clusters are shown in Figs. 2(a) and (b), respectively, for the endohedral cage and wurtzite structures, while the corresponding bulk geometries before relaxation are shown in Figs. 2(a') and (b'). The result for the endohedral cage structure is the same as that given in Refs. [1-3].

Note that there is no corresponding bulk geometry for the endohedral cage structure in Fig. 2(a).

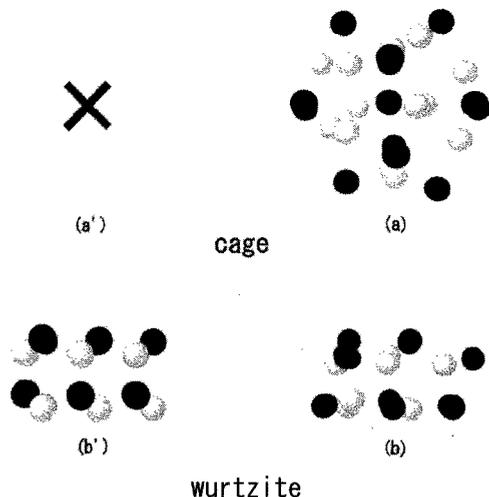


Fig. 2 Optimized $(\text{CdSe})_{13}$ geometries for the (a) endohedral cage and (b) wurtzite structures. Left figures, (a'), (b'), show the corresponding bulk geometries before relaxation (a cross in (a') means that the endohedral cage structure has no bulk counterpart). White and black spheres are Cd and Se atoms, respectively.

Next we performed the calculation of the dielectric function for the two clusters shown in Figs. 2(a) and (b). For this purpose, we used the all-electron mixed basis approach [5-7], in which each LDA wave function is expanded in the linear combination of both atomic orbitals (AO's) and plane waves (PW's). We used an

fcc lattice with the unit cell size corresponding to the nearest neighbor distance between clusters being equal to a . All core and valence AO's are generated by Herman-Skillman's atomic code [8] within the non-overlapping atomic spheres, and the 4 Ry is assumed for the PW's. The dielectric function is evaluated within the random phase approximation (RPA) via the equation [9]

$$\epsilon(q, \omega) = 1 - \frac{8\pi}{\Omega q^2} \sum_k \sum_{\lambda} \sum_{\nu} \frac{\left| \langle k+q, \lambda | e^{iq \cdot r} | k, \nu \rangle \right|^2 [f_0(\epsilon_{k+q, \lambda}) - f_0(\epsilon_{k, \nu})]}{\epsilon_{k+q, \lambda} - \epsilon_{k, \nu} - \omega - i\delta}, \quad (1)$$

where the summations with respect to the level indices λ and ν run over all levels (here we chose 1,000 levels), k is the wave vector inside the first Brillouin zone and denotes f_0 the Fermi-Dirac distribution function; the prefactor 2 means the spin multiplicity and Ω is the volume of the unit cell.

4. RESULT

Figs. 3(a) and (b) show our results of the dielectric function for the endohedral cage structure and wurtzite structure, respectively.

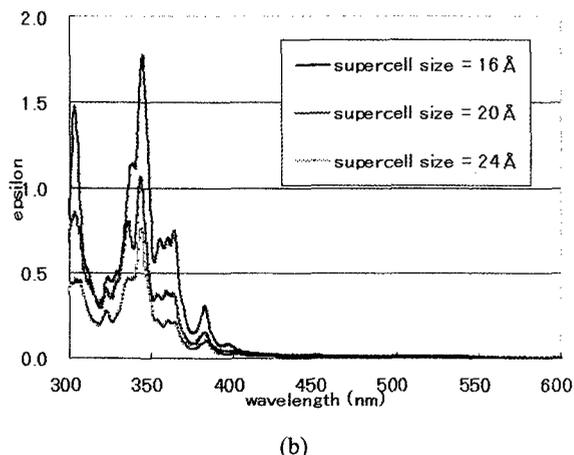
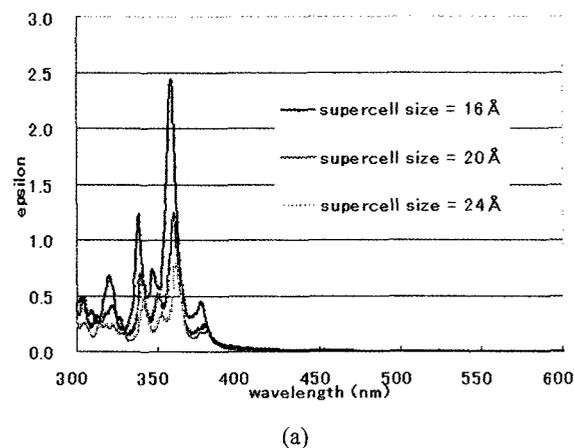


Fig. 3 Imaginary part of dielectric function of $(\text{CdSe})_{13}$ clusters for (a) the endohedral cage and (b) the wurtzite structures. In the figures, three curves (from top to bottom) represent the results for different supercell sizes, 16 \AA , 20 \AA and 24 \AA , respectively.

If we compare three curves in Figs. 3 (a) and (b), we find that the effect of the supercell size is not negligible, because the peaks of supercell size = 16 Å are much higher than those of supercell size = 24 Å. The larger the intercluster distance, the lower the height of the peaks. This is mainly because of the factor $1/\Omega$ in Eq.(1).

The peak positions are, however, not sensitive to the supercell size. In Fig. 3(a) for the endohedral cage structure, there are two peaks around 340nm and 360nm. On the other hand, the results for the wurtzite structure in Fig. 3(b) have the following characteristics:

- (1) Two peaks around 300-310nm and 340nm.
- (2) Shoulder around 350-360nm.
- (3) Long tail in lower energy side.

The shoulder of (2) may correspond to the right side of the experimental peaks around 350nm of lower curves in Fig. 1.

5. INTERPRETATION OF EXPERIMENT

Based on the fair agreements between theoretical calculation and experimental results, the observed spectra are interpreted as follows:

From the above result, under light illumination the certain number of clusters having cage like structure decomposes by a well-known effect of size selective photoetching. This seems to have a linear character with respect to the time of light illumination. The more the time of illumination, the more clusters decompose and a part of the rest of clusters changes the geometry from cage structure to wurtzite structure. It effects as well as to the local arrangement of the organic molecules surrounding $(\text{CdSe})_{13}$ which changes due to the electric fields caused by the charged rest of $(\text{CdSe})_{13}$ clusters. Then, we would imagine that the rest of clusters, solvent and surfactants molecules gradually rearrange their positions and structure to stabilize whole system.

The decrease of number of clusters leads to the increase of effective distance between $(\text{CdSe})_{13}$ clusters. Then, we could argue that the upper curves observed for low illumination times correspond to the samples that have a short intercluster distance and are characteristic of the endohedral cage structure, while the lower curves observed for long times illuminations correspond to the samples which have a large intercluster distance and are characteristic of wurtzite structure.

6. SUMMARY

In summary, we have optimized two (endohedral cage and wurtzite) structures of $(\text{CdSe})_{13}$ and calculated their

dielectric response function in the RPA on the basis of the LDA in density functional theory. We have compared its imaginary part with the optical absorption spectra measured experimentally for the $(\text{CdSe})_{13}$ sample dissolved in toluene. We conclude that most of the created clusters in solution have the endohedral cage structure. The experimental results show some aging effect of sample as noted in the optical spectrum. It may be caused by a change in the geometry of the clusters from the endohedral cage structure to the wurtzite structure. For this explanation, our theoretical results are consistent with the experimental observations. More experimental investigation, however, is necessary for sample preparation to discuss further. The calculations for the larger size cluster, of $(\text{CdSe})_{33}$ and $(\text{CdSe})_{34}$ are now on progress and will be reported in near future.

7. ACKNOWLEDGEMENT

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REFERENCES

- [1] Y. Barnakov, R. Sivamohan, I. Dimitruk, T. Kudo, T. Nirasawa, T. Arai, K. Tohji, O. Terasaki, A. Kasuya, V. Kumar and Y. Kawazoe, Proc. Int. Symp. On Cluster Assembled Mater. (IPAP Conf. Series 3) pp. 56-58 (2002).
- [2] A. Kasuya, R. Sivamohan, Y. Barnakov, I. Dimitruk, T. Nirasawa, S. Mamykin, V. Romanyuk, K. Tohji, V. Jeyadevan, K. Shinoda, T. Kudo, O. Terasaki, Z. Liu, V. Kumar, R. Belosludov, V. Sundararajan, and Y. Kawazoe, to be published.
- [3] V. Kumar, R. Belosludov, V. Sundararajan, Y. Kawazoe, and A. Kasuya, to be published.
- [4] G. Kresse and J. Furthmüller, Comput. Mater. Sci. 6, 15 (1996); Phys. Rev. B 54, 11 169 (1996).
- [5] K. Ohno, Y. Maruyama, K. Esfarjani, Y. Kawazoe, N. Sato, R. Hatakeyama, T. Hirata and M. Niwano, Phys. Rev. Lett. 76, 3590 (1996).
- [6] K. Ohno, F. Mauri and S. G. Louie, Phys. Rev. B 56, 1009 (1997).
- [7] S. Ishii, K. Ohno and Y. Kawazoe, Mater. Trans. JIM 40, 1209 (1999).
- [8] F. Herman and S. Skillman, "Atomic Structure Calculations" (Prentice-Hall, New Jersey, 1963).
- [9] S. L. Adler, Phys. Rev. 126, 413 (1962).

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