PRL 103, 047402 (2009) PHYSICAL REVIEW LETTERS week ending 24 JULY 2009

Optical Response of Diamond Nanocrystals as a Function of Particle Size, Shape, and Symmetry

Lasse Landt,[1] Kathrin Klünder,[1] Jeremy E. Dahl,[2] Robert M. K. Carlson,[3] Thomas Möller,[1] and Christoph Bostedt[1,*]

[1]*Institut für Optik und Atomare Physik, Technische Universität Berlin, Eugene-Wigner Building EW 3-1, Hardenbergstr. 36, 10623 Berlin, Germany*

[2]*Geballe Laboratory for Advanced Materials, Stanford University, Stanford, California 94305, USA*

[3]*MolecularDiamond Technologies, Chevron, P. O. Box 1627, Richmond, California 94802. USA*

(Received 25 February 2009; published 23 July 2009)

The optical spectra of hydrogen-passivated diamond clusters (diamondoids) precisely defined in size and shape have been measured in the gas phase, i.e., under an environment similar to boundary conditions typically assumed by theory. Characteristic optical properties evolve for these wide band-gap semiconductor nanocrystals as a function of size, shape, and symmetry in the subnanometer regime. These effects have not previously been theoretically predicted. The optical response of the tetrahedral-shaped $C_{26}H_{32}$ diamond cluster [1(2,3)4] pentamantane is found to be remarkably similar to that of bulk diamond.

DOI: 10.1103/PhysRevLett.103.047402 PACS numbers: 78.67.Bf, 73.22.−f, 78.66.Db, 81.05.Uw

The tunable optical gap of reduced dimensional systems has been a fascinating focus of nanoscale research [1]. Size dependent optical gaps and confinement of exciton states have been observed in a large variety of elemental [2,3] and compound semiconductor nanocrystals [4]. For these systems, virtually all experimental investigations have been performed on samples exhibiting a size distribution, with unknown surface reconstructions, and often deposited on substrates. Theory, on the other hand, typically assumes ideal boundary conditions of single, perfect, isolated, and neutral particles [5–7].

For small metal clusters, conditions conducive to agreement between theory and experiment have been obtained [8]. Similarly, for semiconductors, advances have been made by size selecting and shape resolving charged clusters [9]. The investigation of neutral nanocrystals, however, is of particular interest because the electronic structure and optical properties are expected to converge on those of bulk materials with increasing particle size.

The particle shape has been recognized as an important parameter in determining the optical properties of nanocrystals [10]. To date, experiments on neutral semiconductor particles have been limited to aspect ratios of rather large particles [11]. This was mostly due to the unavailability of nanoparticles with the same chemical makeup and distinct, well-defined variations in shape and size.

In this Letter, we present optical data for a series of size and shape-selected diamond clusters (diamondoids) [12]. These diamond clusters consist of face-fused crystal cages that are perfectly superimposable on the bulk diamond crystal lattice. At the cluster surface, the sp^3-hybridization characteristic for the diamond lattice is retained through complete hydrogen passivation. The experiments described here were performed on a variety of neutral nanodiamond species in the gas phase. Thus, the data were obtained under boundary conditions similar to those typically assumed in theoretical investigations. We find that characteristic optical properties evolve for similarly sized diamond nano-wire, -sheet, and -crystal already in the subnanometer size regime. This shape dependence has not yet been described theoretically. Besides their fundamental interest, the current findings are contributing to the technological potential of these new nanodiamond materials [13–15]. Further, small diamondoids have been found to luminesce in the ultraviolet, making them prospective candidates for optoelectronic applications [16].

The diamondoids used in this work were isolated and purified from petroleum [12] as higher diamondoids have to date not been synthesized [13]. Higher diamondoids were obtained by vacuum distillation above 345 °C and are pyrolyzed at 400° to 450 °C to remove nondiamondoid hydrocarbons. Size and shape selectivity occurred via high-performance liquid chromatography [12]. All samples exhibit purities exceeding 99%, and their structures are confirmed by single crystal x-ray diffraction.

The investigated structures are depicted in Fig. 1. Each solid arrow stands for the addition of four carbon atoms which, as a general rule, corresponds to one additional diamond cage unit. For the discussion of the optical properties, the investigated diamondoids are categorized according to the growth scheme in Fig. 1. For the smallest three structures with 10–18 carbon atoms comprising 1 to 3 cages (left column in Fig. 1), only a single isomer exists. They are referred to as *molecular structures*. For the next diamondoid size (middle left column), the additional diamondoid cage can be added at three different sites resulting in three different isomers with 22 carbon atoms. Because each of these isomers can be regarded as basis for further growth into a distinguished geometry, they are denoted *transitional structures*. Each of the three largest investigated diamondoids with 26 carbon atoms (middle right column) is the first representative of a basic geometry,

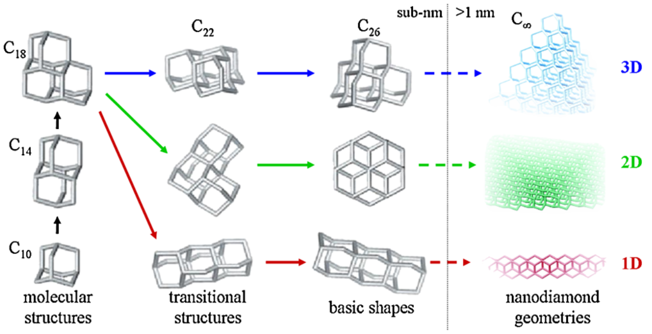

FIG. 1 (color online). Investigated diamondoids categorized by their size and divided into different geometrical families (3D, 2D, 1D). The two middle columns contain clusters of same size. Following the arrows distinguished geometries evolve representing 3D, 2D, 1D nanostructures. Only the carbon framework is shown; the hydrogen termination is omitted for clarity.

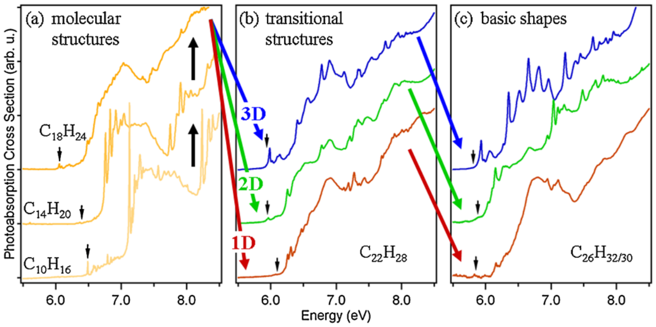

FIG. 2 (color online). Optical absorption as a function of cluster size and shape. The spectra are arranged corresponding to the structures shown in Fig. 1. The optical gaps are indicated by small arrows.

e.g., a tetrahedron, disc, and wire nanocrystal. They are therefore referred to as *basic shapes*.

The optical absorption of the diamond clusters is determined as difference of the measured transmission between a filled and an empty absorption cell. The experiments are performed using synchrotron radiation from beam line I of HASYLAB (DESY, Hamburg). The experimental resolution is determined to be better than 0.02 eV. The diamondoids are brought into the gas phase in an absorption cell for high temperature vacuum applications with vacuum-ultraviolet transparent MgF_2 crystal windows. The absorption cell is heated to temperatures of 20°–220 °C which is well within the range of the thermal stability of diamondoids [12]. The vapor pressures in the absorption cell are on the order of 10 Pa. Prior to the measurement the samples are outgassed in vacuum ($\sim 10^{-4}$ Pa) at elevated temperatures and no buffer gas is used.

The absorption data are shown in Fig. 2. The spectra are arranged corresponding to the structures depicted in Fig. 1. The overall optical absorption of the diamond clusters changes strongly as a function of their size and shape, reflecting the geometric classifications described above. For the three smallest diamondoids [adamantane, diamantane, triamantane; Fig. 2(a)] a transition from discrete, molecularlike excitations into smooth, quasicontinuous spectra is observed. This sudden transition cannot be solely explained by thermal broadening as average thermal energies increase from only 32 to 37 meV. The spectrum of the smallest diamondoid with a single cage, $C_{10}H_{16}$ (adamantane), exhibits numerous sharp features, the most prominent of which have been identified as Rydberg states [17]. Diamantane with 2 diamond cages displays similar features. An assignment of peaks to a specific Rydberg series is no longer possible. The sharp resonances vanish completely when a third cage is added.

As one examines the spectra of larger diamond clusters, following the arrows in Fig. 2, distinct spectra evolve within each structural family. The 3-dimensional family, displayed in the top row of Fig. 2, shows strong resonances at the absorption onset and five sharp almost equidistant peaks emerge. In contrast, the absorption onset of the 2D family, shown in the middle row, is rather smooth and overall the spectra exhibit relatively few features. The spectra of the 1D family (rods or wires) are smooth over most of the energy range with only sporadic appearance of spectral structure. The absorption onset consists of a continuous increase rather than a distinguishable single absorption peak. For the larger cluster sizes, the high symmetry 3D structure shows the most pronounced spectral features corresponding to the most degenerate electronic structure. The data show that for stoichiometrically identical diamond clusters, the optical properties depend sensitively on the atomic configuration of the structural isomer, i.e., shape.

The absorption onset of the nanocrystals determines their optical gap. The gap can be defined as a small but nonzero fraction of the integrated oscillator strength. This method has the advantage of being applicable to both theory and experiment [6,18]. Figure 3(a) presents the integrated oscillator strength for the investigated diamondoids, normalized to the value at the ionization potential [19]. The data allow us to set the threshold for the optical gap at a fraction of 5×10^{-4} of the normalized oscillator strength [dashed line in Fig. 3(a)] which is comparable to values used in theoretical studies [6]. Two main effects dominate the experimental error of the optical gaps: the reproducibility of the measured spectra and the experimental values for the ionization potentials [19] used to normalize the integrated oscillator strength. They each result in an uncertainty of about 5 meV. Considering the beam line resolution of 20 meV, the presented gap values can be estimated to be accurate within 30 meV. The resulting optical gaps are marked with arrows in the spectra in Fig. 2 and are summarized in Fig. 3(b) as well as Table I. The optical gap values exhibit a clear deviation from a simple scaling of the gap with the number of atoms for the $C_{14}H_{20}$ cluster (diamantane) and the 1D transitional structure with 22 carbon atoms ([121]tetramantane). These

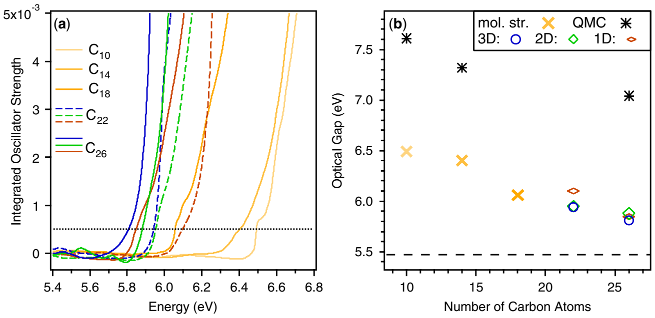

FIG. 3 (color online). (a) Integrated oscillator strength for the measured diamond clusters. The threshold defining the optical gap is marked by a dotted line. (b) Optical gaps as function of size. The experimental gaps are compared to optical gaps derived by QMC calculations [21]. The dashed line marks the energy gap of bulk diamond [30].

irregularities coincide with the lack of pronounced spectral features at the absorption onset. Interestingly, for the basic shapes (26 carbon atoms, panel c), a pronounced resonance at the gap is only clearly observable for the 3D structure, and the gap values are similar for all isomers.

For comparison, computed gap values of recent quantum Monte Carlo (QMC) calculations explicitly tailored to yield optical gaps of diamondoids [21] are added to Fig. 3(b). The theoretically predicted gaps are more than 1 eV too large, overestimating the quantum size effects by 100% to 300%. Furthermore, the irregularity for the second smallest cluster is not observed in the QMC data. Efforts to calculate the optical spectra of small nanodiamonds using time-dependent density functional theory [22] fail to reproduce the well-known spectra of the smallest cluster [17] and the quantum size effects for structures similar to the ones in this work seem largely overestimated. Deviations of comparable extent are found for previous experimental band edge investigations [23] and other theoretical work [24,25]. However, these studies focused on band edge shifts rather than optical transitions; thus, the comparability is limited.

TABLE I. Optical gaps for all measured diamondoids. Names in the Balaban-Schleyer nomenclature [20] are listed with the chemical formula. Cat. refers to categories introduced in the text: *M* denotes molecular structure, *T* transitional structure, and *B* basic shape. Symmetry is given in Schönflies notation.

Diamondoid Name	Formula	Cat.	Sym.	Gap [eV]
adamantane	$C_{10}H_{16}$	*M*	T_d	6.49
diamantane	$C_{14}H_{20}$	*M*	D_{3d}	6.40
triamantane	$C_{18}H_{24}$	*M*	C_{2v}	6.06
[1(2)3]tetramantane	$C_{22}H_{28}$	*T* (3D)	C_{3v}	5.94
[123]tetramantane	$C_{22}H_{28}$	*T* (2D)	C_2	5.95
[121]tetramantane	$C_{22}H_{28}$	*T* (1D)	C_{2h}	6.10
[1(2,3)4]pentamantane	$C_{26}H_{32}$	*B* (3D)	T_d	5.81
[12312]hexamantane	$C_{26}H_{30}$	*B* (2D)	D_{3d}	5.88
[1212]pentamantane	$C_{26}H_{32}$	*B* (1D)	C_{2v}	5.85

To investigate the correlation between the gap value and the absorption onset, symmetry selection rules governing optical transitions are considered. For this purpose, the orbital symmetries are calculated at B3LYP/6-31G* level of theory [26] using GAUSSIAN03 [27]. For those structures which behave irregularly, the lowest transitions are symmetry-forbidden. In the case of the 1D transitional structure belonging to the C_{2h} point group, transitions from highest occupied molecular orbitals (HOMO, HOMO-1, and HOMO-2) to the lowest unoccupied molecular orbital (LUMO) are forbidden. This is also true for the HOMO-LUMO and (HOMO-1)-LUMO transitions of the two-cage $C_{14}H_{20}$ diamantane, exhibiting D_{3d} symmetry. Interestingly, the lowest transitions for the 2D basic shape are also symmetry-forbidden. While this is also reflected in the spectra, showing a smooth absorption onset, its absolute gap value exhibits only a minor deviation from the other two basic shapes. In this context, it should be noted that of all samples, the 2D basic shape is measured at the highest temperature. Therefore phonon-assisted transitions may play a role in lowering the measured gap. The allowed HOMO-LUMO transitions for all other diamondoid structures coincide with an accentuated single or double peak at their absorption onset defining the optical gap. This spectral feature can thus be assigned to transitions from the HOMO into the LUMO which is defined by the hydrogen surface [28]. This interpretation is in agreement with calculations predicting optical gaps of larger hydrogen-passivated nanodiamonds to lie below the bulk value due to such surface states [29].

The closest related system to the presently investigated diamond clusters are hydrogen passivated silicon nanocrystals. Various theoretical approaches have been applied to the problem of optical gaps and spectra for these systems [5–7]. The sudden transition from sharp, distinct features to smooth spectra, as presently found for diamondoids going from two to three crystal cages, has not been reported [6]. Furthermore, the spectra are predicted to become more continuous with increasing size even for highly symmetric, spherical Si-nanocrystals [6]. These predictions contrast our results of a spectrum with strong, equally spaced resonances for the highly symmetric 3D basic shape.

The optical absorption of the 3D basic shape (compare Fig. 1) shows a surprising similarity to that of bulk diamond [30] suggesting that this tetrahedral nanodiamond ([1(2,3)4]pentamantane) can, in many respects, be considered the smallest diamond [31]. In Fig. 4, the nanocrystal's spectrum has been shifted by 0.73 eV to overlay with the spectrum of bulk diamond in order to account for quantum size effects. Both spectra exhibit strong resonances with equal energy spacing. A resemblance to the bulk spectrum is only observed for the 3D basic shape with T_d symmetry which is the largest finite subgroup of the infinite O_h bulk diamond symmetry group. The growing intensity deviation towards higher energies is due to the different applied methods of transmission and luminescence yield absorption measurements [30]. The two spectra differ in relative

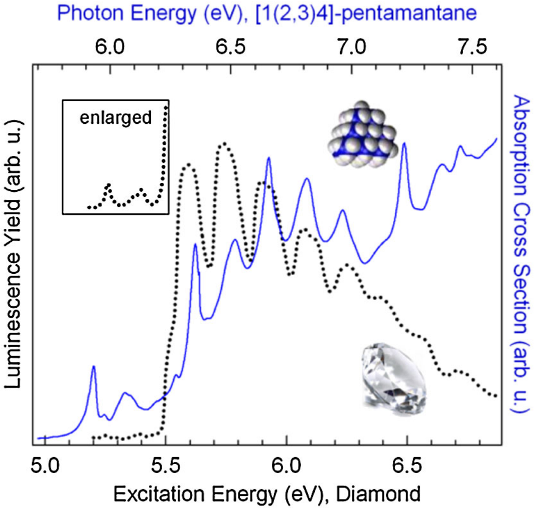

FIG. 4 (color online). Comparison of the optical absorption of the 3D *basic shape* ([1(2,3)4]pentamantane) with the absorption of high purity type IIa diamond (dotted line) [30]. The spectra are plotted over different axes which are shifted by 0.73 eV. The spectral inset shows the enlarged onset of the bulk diamond spectra.

intensity of the pre-edge spectral features. For bulk diamond, an indirect, wide band-gap semiconductor, these transitions have been related to impurities, so-called N9-centers [32]. In the defect-free nanodiamond, they must be ascribed to transitions into the LUMO defined by the hydrogen surface [28] as discussed above. The difference in relative intensities for the bulk and nanocrystal samples is due to their different surface-to-bulk ratio.

In conclusion, the optical response of diamond clusters is determined by an interplay of size, shape, and symmetry. The data show that for each of the diamond growth branches towards 1D, 2D, and 3D structures, characteristic optical properties evolve. They reveal irregularities of gap evolution with cluster size that can be attributed to symmetry constraints for the lowest transitions. Theoretical results for optical gaps do not match the current experimental findings with respect to both the absolute and trends in the gap value. Our experimental environment mimics the ideal boundary conditions typically assumed in theoretical electronic structure investigations delivering benchmark data against which competing theoretical approaches may be tested. Comparison of the spectra of the tetrahedral $C_{26}H_{32}$ cluster and bulk diamond shows remarkable similarities suggesting that optical properties of diamond evolve in the sub-nm regime.

This work is supported by the Deutsche Forschungsgemeinschaft DFG. L. L. is grateful for support from the Studienstiftung des Deutschen Volkes. Further, the authors would like to thank J. Maultzsch and M. Mohr for discussion on symmetry.

*Corresponding author: bostedt@physik.tu-berlin.de

[1] L. E. Brus, J. Chem. Phys. **80**, 4403 (1984).
[2] T. van Buuren, L. N. Dinh, and L. L. Chase *et al.*, Phys. Rev. Lett. **80**, 3803 (1998).
[3] C. Bostedt, T. van Buuren, and T. M. Willey *et al.*, Appl. Phys. Lett. **84**, 4056 (2004).
[4] A. P. Alivisatos, J. Phys. Chem. **100**, 13226 (1996).
[5] M. Rohlfing and S. G. Louie, Phys. Rev. Lett. **80**, 3320 (1998).
[6] I. Vasiliev, S. Öğüt, and J. R. Chelikowsky, Phys. Rev. Lett. **86**, 1813 (2001).
[7] L. X. Benedict, A. Puzder, and A. J. Williamson *et al.*, Phys. Rev. B **68**, 085310 (2003).
[8] W. de Heer, Rev. Mod. Phys. **65**, 611 (1993).
[9] M. F. Jarrold and V. A. Constant, Phys. Rev. Lett. **67**, 2994 (1991).
[10] G. D. Scholes and G. Rumbles, Nature Mater. **5**, 683 (2006).
[11] X. Peng, L. Manna, and W. Yang *et al.*, Nature (London) **404**, 59 (2000).
[12] J. E. Dahl, S. G. Liu, and R. M. K. Carlson, Science **299**, 96 (2003).
[13] A. P. Marchand, Science **299**, 52 (2003).
[14] W. L. Yang, J. D. Fabbri, and T. M. Willey *et al.*, Science **316**, 1460 (2007).
[15] Y. Wang, E. Kioupakis, and X. Lu *et al.*, Nature Mater. **7**, 38 (2008).
[16] L. Landt, W. Kielich, and D. Wolter *et al.* (to be published).
[17] J. W. Raymonda, J. Chem. Phys. **56**, 3912 (1972).
[18] R. Schäfer and J. A. Becker, Phys. Rev. B **54**, 10296 (1996).
[19] K. Lenzke, L. Landt, and M. Hoener *et al.*, J. Chem. Phys. **127**, 084320 (2007).
[20] A. T. Balaban and P. von R. Schleyer, Tetrahedron **34**, 3599 (1978).
[21] N. D. Drummond, A. J. Williamson, R. J. Needs, and G. Galli, Phys. Rev. Lett. **95**, 096801 (2005).
[22] J.-Y. Raty and G. Galli, J. Electroanal. Chem. **584**, 9 (2005).
[23] T. M. Willey, C. Bostedt, and T. van Buuren *et al.*, Phys. Rev. B **74**, 205432 (2006).
[24] G. C. McIntosh, M. Yoon, S. Berber, and D. Tománek, Phys. Rev. B **70**, 045401 (2004).
[25] A. J. Lu, B. C. Pan, and J. G. Han, Phys. Rev. B **72**, 035447 (2005).
[26] A. A. Fokin, B. A. Tkachenko, P. A. Gunchenko, D. V. Gusev, and P. R. Schreiner, Chem. Eur. J. **11**, 7091 (2005).
[27] M. J. Frisch *et al.*, Gaussian 03, Revision C. 02 (Gaussian, Inc., Wallingford, CT, 2004).
[28] T. M. Willey, C. Bostedt, and T. van Buuren *et al.*, Phys. Rev. Lett. **95**, 113401 (2005).
[29] J.-Y. Raty, G. Galli, and C. Bostedt *et al.*, Phys. Rev. Lett. **90**, 037401 (2003).
[30] P. J. Dean and J. C. Male, Proc. R. Soc. A **277**, 330 (1964).
[31] A. A. Fokin, P. R. Schreiner, and N. A. Fokina *et al.*, J. Org. Chem. **71**, 8532 (2006).
[32] P. Denham, E. C. Lightowlers, and P. J. Dean, Phys. Rev. **161**, 762 (1967).