

Quantum confinement observed in the X-ray absorption spectrum of size distributed nanodiamonds extracted from the Murchison meteorite T. Berg¹, E. Marosits², J. Maul¹, P. Nagel³, U. Ott², F. Schertz¹, S. Schuppler³, Ch. Sudek² and G. Schönhense¹, ¹Institut für Physik, Staudingerweg 7, D-55128 Mainz, Germany, ²Max-Planck-Institut für Chemie, Becherweg 27, D-55128 Mainz, Germany, ³Forschungszentrum Karlsruhe, Institut für Festkörperphysik (IFP), D-76021 Karlsruhe, Germany.

Introduction: Quantum confinement effects in semiconductor nanoparticles were discovered more than two decades ago [1] and have attracted increasing interest during recent years [2-4]. Influence of particle size on the energy levels of excitons and conduction band edges were verified for a variety of nanoscaled materials, e.g. small structures of silicon, germanium and indium phosphide. In the field of nanotechnology, applications such as quantum dots and quantum wires were developed, depending on the dimensionality of the spatial boundary conditions. Confined structures are characterized by a sharper density of states compared to higher-dimensional objects which plays an important role in the design of a multiplicity of devices like diode lasers, biological sensors and solid state quantum computers. In addition, quantum confinement is revealed by a blue shift of energy levels with decreasing particle size. Among these features are conduction band edges manifested as absorption edges and exciton peaks in spectroscopic investigations. In the case of nanodiamonds, evidence for quantum confinement was reported by Chang et al. in 1999 [5], but the discussion about the extent of this effect in nanosized diamond crystals is still ongoing [6-8].

We report on near edge X-ray absorption fine structure (NEXAFS) measurements of the carbon K-edge of artificial micron sized diamonds and of meteoritic nanodiamonds (C δ). In comparison to bulk diamond, the NEXAFS spectrum of Murchison C δ nanodiamonds shows a blue shifted, asymmetric and broadened exciton peak. The effect of broadening observed in studies of terrestrial nanodiamonds has been associated with the particle size distribution in recent publications, e.g. [9], but a detailed explanation is still missing. We present a quantitative analysis of the modified peak shape of the C 1s core exciton and of the modified carbon K-edge. This modification is caused by the interplay between the size distribution [10] and quantum confinement.

Experiment: Imaging NEXAFS measurements were performed at the soft X-ray beamline WERA at the synchrotron light source ANKA (FZ Karlsruhe). The samples were illuminated with monochromatized radiation with energies between 277 eV and 310 eV covering the carbon K-edge region (see Fig.1). The lateral distribution of the emitted electron intensity was

mapped by means of a photoemission electron microscope (FOCUS IS-PEEM).

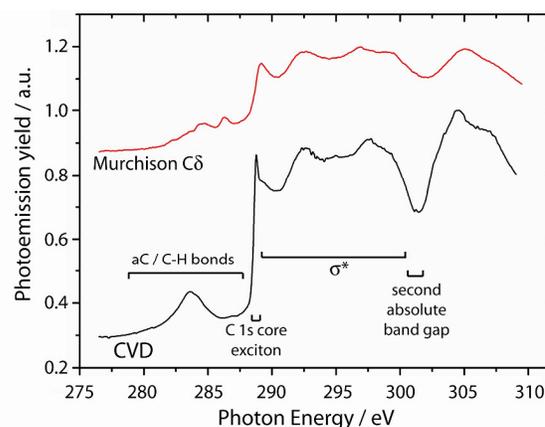


Fig.1 Comparison of the NEXAFS spectra of artificial CVD-diamonds with Murchison C δ nanodiamonds. The C δ spectrum shows a C 1s core exciton peak, which was not detected during previous investigations of meteoritic nanodiamonds [11,12].

XAS-Analysis: Excitonic states in semiconductor crystals result from the formation of bound electron-hole pairs. The size of these quasiparticles, so-called Mott-Wannier-type excitons, is much larger than the interatomic distance in the crystal lattice and is characterized by an effective Bohr radius that crucially depends on material properties. Quantum confinement effects arise if the Bohr radius of the exciton is affected by the spatial boundary conditions of the host particle when reaching a critical size. Its deformation increases with decreasing particle size and is revealed by an increasing energy of the exciton. Additionally, the conduction band edge is shifted to higher energies which can be detected as a blue shift of the onset of the X-ray absorption edge. The energy shifts for excitons and for the conduction band edge are both given within the Effective Mass Approximation (EMA) theory by

$$E(r) = E_{re} + \frac{\hbar^2 \pi^2}{2m^*} \frac{1}{r^2}$$

Here, E_{re} represents the unshifted reference energy in the bulk, and r is the radius of the particle. For analysis of the conduction band edge, m^* is identified with the effective electron mass m_e^* , and in the case of the exci-

ton, m^* corresponds to the effective electron-hole pair mass m_{e-h}^* .

Chang et al. have determined the effective electron mass (in units of the electron mass m_e) in nanodiamonds as $m_e^* = 0.1m_e$ [5]. This value will be used during analysis.

Watanabe et al. [13] determined the exciton Bohr radius of bulk diamond as 1.57 nm. This small value suggests the occurrence of quantum confinement effects in diamond nanoparticles, and ensures bulk-like behavior for the micron size CVD diamonds. For bulk diamond, the conduction band edge is described by an arctangent step function (step width Γ_S) [5]; the exciton peak is described by a Lorentzian with natural lifetime $\tau_L \sim 1/\Gamma_L$.

$$f_{bulk}(E) \propto \frac{\left(\frac{\Gamma_L}{2}\right)^2}{(E - E_{re,L})^2 + \left(\frac{\Gamma_L}{2}\right)^2} + \arctan\left[\frac{E - E_{re,S}}{\Gamma_S/2}\right]$$

$E_{re,L}$ and $E_{re,S}$ are the bulk reference energies of the exciton and of the absorption edge.

The Murchison C δ nanodiamonds exhibit a lognormal size distribution $L(r)$ with a median effective particle radius of $\langle r \rangle = 1.3$ nm (corresponding to ~ 1600 carbon atoms) as known from e.g. [10]. Assuming quantum confinement, different particle sizes cause different energy shifts of the carbon K-edge and of the C 1s core exciton. Therefore, the near edge X-ray absorption spectrum of nanodiamonds is obtained from the convolution of the bulk X-ray absorption spectrum f_{bulk} with the “energy distribution” of the nanoparticles \tilde{L} :

$$f_{nano}(E) = (f_{bulk} * \tilde{L})(E) = \int_{E_{re}}^{\infty} f_{bulk}(E') \cdot \tilde{L}(E - E') dE'$$

The values for the bulk reference energies E_{re} of the exciton and of the X-ray absorption edge $E_{re,L}$ and $E_{re,S}$ are extracted from the bulk CVD diamond fitting curve and serve as input for the numerically evaluated nanodiamond fitting function. The corresponding widths Γ_L , Γ_S and the effective exciton mass m_{e-h}^* are treated as free parameters. The value for m_e^* has been taken from [5], those for μ and σ describing the shape of the lognormal size distribution from [10].

Applying a least squares fitting of f_{bulk} to the onset of the carbon K-edge of the CVD diamond spectrum, Γ_L , Γ_S and the bulk reference energies $E_{re,L}$ and $E_{re,S}$ are obtained. The fitting function is shown in Fig.2a in comparison to the measured data. The two components describing the Lorentzian shaped exciton and X-ray absorption edge are plotted in the insert in addition. In Fig.2b, the blue shifted, asymmetric and broadened onset of the carbon K-edge of the C δ nanodiamond

spectrum is shown for comparison. Utilizing the bulk reference energies, and the literature values for μ , σ and m_{e-h}^* , the fitting curve is obtained by varying the three free parameters Γ_L , Γ_S and m_{e-h}^* .

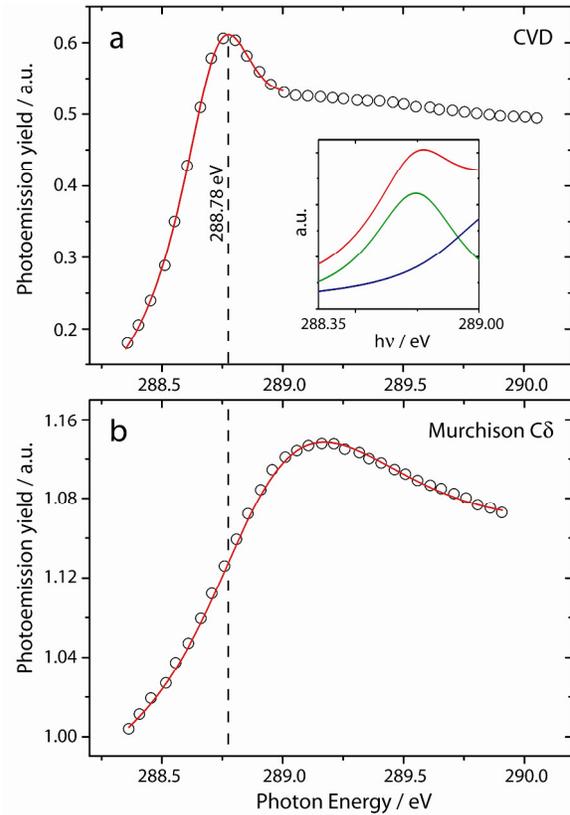


Fig.2 Comparison of the measured data (open circles) with the deduced fitting functions (solid curves).

The fitting curve reproduces the measured data with high precision which supports the idea of quantum size effects in nanodiamonds, as originally proposed by [5]. This project is supported by DFG (SCHO 341/10-1).

References: [1] Brus L. (1986) *J. Phys. Chem.*, 90, 2555-2560. [2] Hill N.A. et al. (1995) *Phys. Rev. Lett.*, 75, 1130-1133. [3] Glinka Y.D. et al. (2001) *Phys. Rev. B*, 64, 085421. [4] Raty J.-Y. et al. (2003) *Phys. Rev. Lett.*, 90, 037401. [5] Chang Y.K. et al. (1999) *Phys. Rev. Lett.* 82, 5377-5380. [6] Ley L. et al. (2000) *Phys. Rev. Lett.* 84, 5679-5679. [7] Pong W.F. et al. (2000) *Phys. Rev. Lett.* 84, 5680-5680, [8] Willey T.M. et al. (2005) *Phys. Rev. Lett.* 95, 113401. [9] Tang Y.H. et al. (2003) *Chem. Phys. Lett.* 372, 320-324. [10] Lewis R.S. et al. (1989) *Nature* 339, 117-121. [11] Flynn G.J. (2000) *LPS XXXI*, Abstract #1904. [12] Garvie L.A.J. (2006) *MAPS* 41, 667-672. [13] Watanabe H. et al. (2006) *Diam. Relat. Mater.* 15, 554-558.