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Synchrotron X-Ray Photoemission and Reflectance Study of the Dipole Forbidden Diamond Core Exciton

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The diamond 1*s* core level absorption spectra measured with x-ray reflectance and partial photoelectron yield are compared. A steep rise and a feature around 290 eV in the partial yield are absent in the reflectance. This anomaly in the partial yield is due to the predominance of the Auger yield over the core exciton decay. A binding energy of 1.25 eV for a dipole forbidden core exciton is determined from these spectra. The spectral assignments of absorption features are revised, and discrepancies in diamond core exciton models are resolved.

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Core excitonic effects are important many-body phenomena that affect the optical absorption in insulators and semiconductors. A core exciton does not correspond to a free electron at the bottom of the conduction band and to a hole in the core level, but to a bound electron-hole pair. This produces sharp lines in the absorption spectrum below the core-level threshold. Excitonic effects have been studied for years because of their fundamental interest [1-10]. Diamond is one of the simplest and most important systems in condensed matter. In 1985 Morar and co-workers observed the 1*s* core exciton of diamond at 289.0 eV using partial photoelectron yield [5]. They used the hydrogenic effective mass theory (HEMT) and found an exciton binding energy of 0.2 eV. In 1991 Jackson and Pederson proposed a new theoretical model for diamond 1*s* core exciton [7]. They noted that the diamond $1s\text{-}A_1$ core exciton should have a binding energy of about 1.6 eV, by analogy to the nitrogen donor level. They concluded that the $1s\text{-}A_1$ core exciton should be dipole forbidden, and the observed feature might be a $1s\text{-}T_2$ exciton [7]. We assign this feature to the $1s\text{-}A_1$ excitonic transition and argue why this transition is observed in the diamond core spectra. We present new experimental evidence that the binding energy of this core exciton feature is 1.25 eV rather than 0.2 eV, as previously thought. This evidence, obtained by comparing synchrotron x-ray reflectance and partial-yield spectra, eliminates a puzzling discrepancy between theory and experiment, concerning this fundamental many-body effect in one of the most important covalent solids. A comparison of the experimental conduction-band transition density of states (CBTDOS) of diamond with band-structure calculations is presented. The spectral assignments of the diamond absorption features are revised and discrepancies in the core exciton models are resolved.

The reflectance and partial-yield experiments were performed at the Naval Research Laboratory's x-ray beam line X24C of the National Synchrotron Light Source (NSLS). In these experiments, a high-resolution grating/crystal monochromator (GCM), an ultrahigh vacuum reflectometer, and a photoelectron spectrometer were used [9]. The photon flux in the beam line at the carbon *K* edge was improved by an oxygen glow discharge cleaning of its optical elements. The incoming x rays were monochromatized using two 2400-groove/mm gold-coated gratings at a blaze angle between 2.5° and 3°. The spectral purity was improved with a titanium filter. The photon energies were calibrated to better than ±0.15 eV by setting the carbon contamination dips in the monochromator flux plot at 285.0 and 291.0 eV [9]. The energy resolution of the reflectometer near the carbon *K* edge was between 0.1 to 0.25 eV.

A yellow, type-IA diamond crystal with a smooth (100) face was boiled in a concentrated sulphuric, nitric, and perchloric acid mixture and rinsed in deionized water. The reflectometer was at a pressure of 2×10^{-9} Torr. The diamond was not heated in vacuum. The diamond reflectance spectra in Fig. 1 were measured at 10° grazing incidence. In the photoemission experiment, the diamond was attached rigidly to a 0.025-mm-thick tantalum foil. It was mounted on an $XYZ\theta$ manipulator in the x-ray photoemission spectroscopy (XPS) chamber at a pressure of 4×10^{-10} Torr. The sample was heated and annealed above 1300 K by sending a current through the tantalum foil. Any charging effects were eliminated by illuminating the sample with a xenon lamp through a quartz window in the XPS chamber. The bulk sensitive diamond 1*s* partial-yield or constant-final-state (CFS) spectra were measured by a double-pass cylindrical mirror analyzer (CMA). The energy window of the CMA was kept at a kinetic energy of 7.5 eV. The monochromator transmission near the carbon *K* edge was measured from the CFS spectrum of the clean tantalum. The diamond CFS spectrum in Fig. 1, curve *d* was normalized using the x-ray absorption coefficient of tantalum and the monochromator transmission.

The x-ray emission spectroscopy (XES) measurements were made at the University of Virginia. A 3-keV electron beam was used to create core holes in a type-IIB diamond. The x rays emitted due to transitions of valence electrons to the core holes were measured as a function of the energy [8]. The energy resolution of the emission

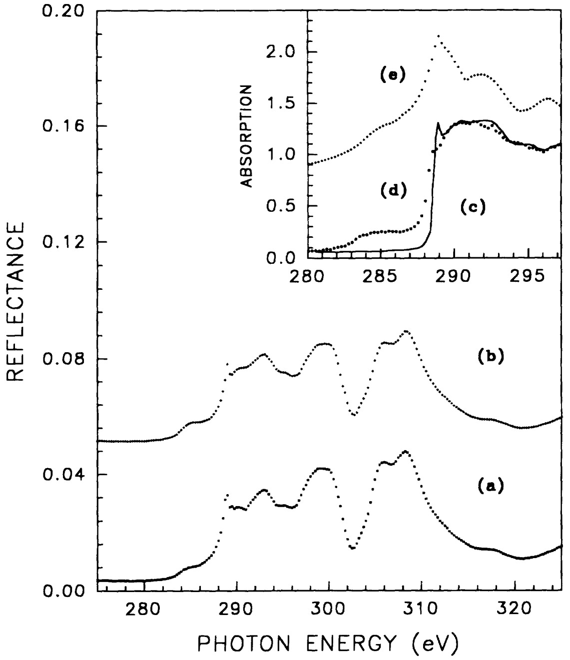

FIG. 1. Curve *a*, the *s*-polarization reflectance, and *b* *p*-polarization reflectance of a type-IA diamond measured at 10° grazing angle of incidence. The *p*-polarization reflectance is shifted vertically by 0.045 unit. Inset: The partial yield of a type-IIB diamond [5] (*c*), and a type-IA diamond (*d*), and the optical absorption of the type-IA diamond derived from its reflectance (*e*).

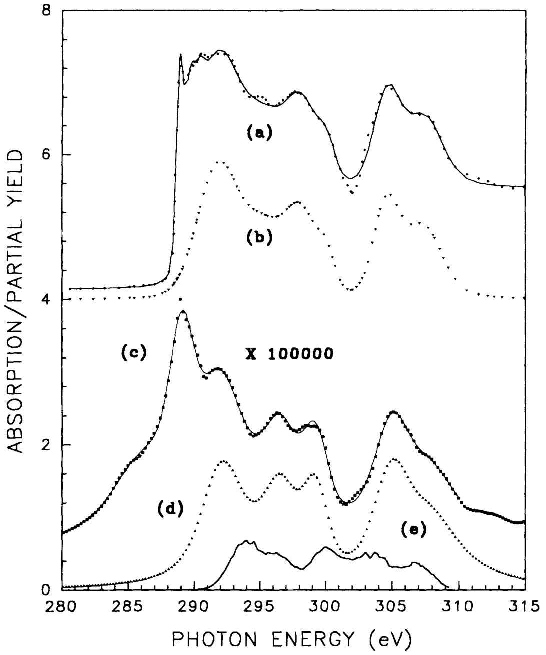

FIG. 2. Curve *a*, the partial yield of a clean annealed type-IIB diamond [5], multiplied and shifted vertically. Line through data points is a model fit. Curve *b*, the CBTDOS of type-IIB diamond obtained from a curve fitted to *a*. Curve *c*, the optical absorption coefficient of type-IA diamond in cm^{-1} derived from reflectance. Line through data points is a model fit. Curve *d*, the CBTDOS of the type-IA diamond obtained from a model fitted to *c*. Curve *e*, the *p*-CBDOS of diamond calculated with a LAPW method [12,15]. The curve was broadened with a Gaussian of width 1.0 eV.

spectrum was between 0.2 and 0.3 eV. The valence-band transition density of states of diamond in Fig. 3 was obtained by dividing the data by an E^3 factor, where E is the photon energy; the resulting curve was normalized to an area of unity between 260 and 290 eV after removing a linear background.

The optical absorption of the type-IA diamond derived from the reflectance using a Kramers-Kronig analysis is shown in Fig. 1, curve *e* and Fig. 2, curve *c*. The accuracy of the absorption coefficient of diamond was verified using various sum rules [11]. The partial yield of the type-IA diamond shown in Fig. 1, curve *d* does not resolve the core exciton at 289.0 eV due to insufficient resolution. The partial yield of a type-IIB diamond of Ref. [5] is shown in Fig. 1, curve *c* and Fig. 2, curve *a*. The optical absorption and reflectance in Fig. 1, curves *a* and *b*, and Fig. 2, curve *c* and the CFS spectra in Fig. 2, curve *a* agree in shape above 294.0 eV; but there are remarkable differences in these spectra from 289.0 to 294.0 eV. A steep rise in the intensity of the CFS spectra just above the core exciton and a broad feature around 290 eV are absent in the optical reflectance and absorption spectra. This anomalous feature in the CFS spectrum was not produced in a multiple scattering calculation of the x-ray-absorption near-edge structure (XANES) of diamond [5,12]. Although the CFS spectra have been found, in general, to have a similarity with the optical absorption, distortions of the photoelectron yield spectrum of BeO slightly exceeding the Be core absorption edge were reported. The distortions in the BeO spectrum are due to the competition of the Auger process with the decay of core exciton [13,14]. The Auger yields of light elements like Be and C are close to unity [15]. The observed anomalous spectral shape, slightly above the core exciton in the CFS spectrum in Fig. 1, curve *d* and Fig. 2, curve *a* is due to the predominance of the Auger yield over the core exciton decay [13–15].

A simple model that describes the absorption spectra was developed. It was used to separate the core exciton and band-gap states from the CBTDOS shown in Fig. 2. This model uses a step function convoluted with a Gaussian to describe the continuum absorption, the smallest number of Voigt functions to describe the gap states, core exciton, and conduction-band states. The Gaussian part of the Voigt function arises from broadening due to the instrument, sample, phonon and other mechanisms [9]. The optical absorption in Fig. 2, curve *c* and the CFS in Fig. 2, curve *a* are synthesized very well by our model. The root mean square deviations of the fits with respect to the mean are less than 3%. The fitting parameters are shown in Table I. The broadening of the absorption edge

TABLE I. The parameters of a model fit to the optical absorption spectrum of a type-IA diamond in Fig. 2, curve *c* are shown. The fitting parameters of a CFS spectrum of a type-IIB diamond of Ref. [5] in Fig. 2, curve *a* are shown in parentheses.

Energy position (eV)	FWHM of peak (eV)	Amplitude
289.00 (288.87)	2.38 (0.53)	2.49×10^5 (0.79)
(289.67)	(1.27)	(0.91)
292.01 (291.80)	3.58 (3.62)	1.52×10^5 (0.69)
296.58 (295.27)	5.25 (3.69)	1.07×10^5 (0.35)
299.17 (298.18)	2.04 (2.85)	9.23×10^4 (0.42)
(300.09)	(1.53)	(0.17)
304.95 (304.61)	2.95 (2.27)	1.22×10^5 (0.48)
307.72 (307.35)	7.07 (3.31)	7.99×10^4 (0.39)
290.23 (290.23)	Conduction-band minimum	

in Fig. 1, curves *d* and *e* is related to nitrogen aggregate impurities or platelet defects in type-IA diamond [16]; and the gap states resolved at 285.4 and 286.2 eV by a curve fitted to curve *c* in Fig. 2 are related to these impurity levels. These features could also have small contributions from the unoccupied π^* diamond surface states, since reflectance measured at grazing incidence has some surface sensitivity [9]. Theoretical studies of nitrogen platelet defect levels in diamond are necessary to confirm these conclusions.

The *p*-CBDOS of diamond calculated using a linear augmented-plane-wave (LAPW) method is shown by Fig. 2, curve *e* [17,18]. This curve was broadened by a Gaussian of width 1.0 eV. This calculation does not include self-energy corrections, and it agrees qualitatively with the experimental CBTDOS of diamond in Fig. 2, curves *b* and *d*. The Δ_c conduction-band minimum is found to be at 290.2 eV from the model fits to the optical absorption and partial-yield spectra. The diamond 1*s* core exciton at 289.0 eV has a binding energy of 1.2 eV, rather than a value of 0.2 eV quoted in Ref. [5]. The peak at 289.7 eV of the curve fitted to curve *a* in Fig. 2 could be the $1s$-T_2 exciton with a binding energy of 0.6 eV and it has contributions from the anomalous Auger yield of carbon [7, 13–15]. The peaks at 292.01 and 296.58 eV of the curve fit are due to conduction-band states at the Γ_{15} and L_1/L_3 symmetry points, respectively [19–21]. The peaks at 299.17, 304.97, and 307.72 eV resolved by the model fit agree with the features of a calculated *p*-CBDOS of diamond [21]. An earlier electron energy loss spectroscopy study of the diamond conduction-band electronic structure assigned incorrectly the valence-band maximum, Δ_c, Γ_{15}, and L_1/L_3 symmetry points at 282.5, 289.0, 290.2, and 292.0 [22].

The upper edge of the diamond valence emission band in Fig. 3 is a long and steep straight line, and it apparently has negligible broadening. The valence-band maximum is at 285.0 ± 0.2 eV with respect to the diamond *K* level. The band gap of diamond is 5.48 eV. The exciton at 289.2 eV is found to have a model-independent binding energy of 1.28 eV. This deeply bound Frenkel exciton is the $1s$-A_1 core exciton [7]. The shallow *p*-like exciton predicted by calculation does not appear in this spectrum [7]. The $1s$-A_1 exciton feature is weak in intensity, partly due to the predominance of the Auger yield over its radiative decay [13–15]. In solids containing light elements, the relationship of the intensity of the core exciton with its binding energy is influenced significantly by the competition of the Auger process with the core exciton decay [4,13–15]. The three major core spectroscopic techniques used here, namely, emission, reflectance, and partial yield, gave a consistent binding energy of 1.25 ± 0.15 eV for the core exciton. The $1s$-A_1 exciton is nearly at the same energy position in the absorption and the emission spectra and therefore the Stoke's shift is negligible and the phonon relaxation is incomplete in diamond.

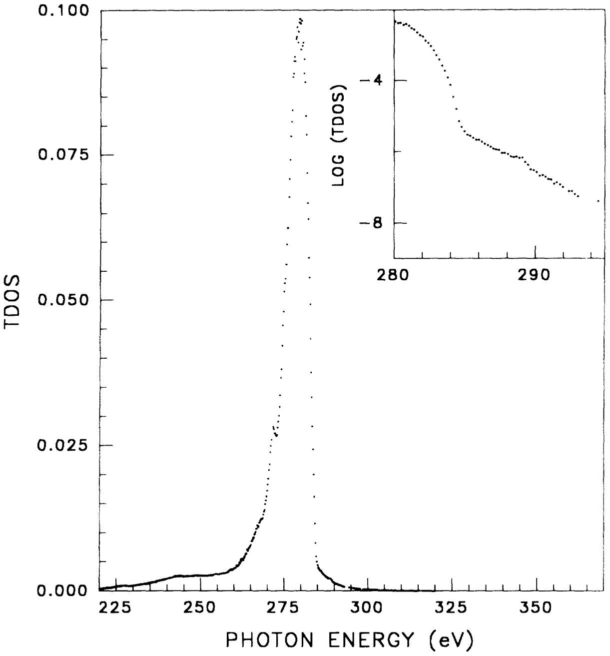

FIG. 3. Diamond valence band TDOS from its *K*-x-ray emission spectrum. Inset: The weak diamond 1*s* core exciton.

The calculation in Ref. [7] did not include the phonon effects and the large Auger yield of carbon. The calculated shape of the diamond *K* absorption in this work disagrees with a multiple scattering calculation of the XANES of diamond [12] and the reflectance and optical absorption spectra in Figs. 1 and 2. The peak at 289.0 eV in the CFS spectrum was assigned incorrectly as the $1s$-T_2 exciton by this theoretical model [7]. The experimental evidence presented here shows that this feature in the absorption and the emission spectra is the deep dipole forbidden $1s$-A_1 exciton. The observation of the dipole forbidden diamond $1s$-A_1 exciton in these spectra is made possible by the intervalley mixing of states at equivalent conduction-band minima and the central cell corrections. Calculations are necessary to study the magnitude of these effects [1,2,23]. The properties of the dipole forbidden diamond core exciton could be further examined using a broken symmetry approach developed for the core hole spectra of semiconductors [3]. We hope that results presented here will stimulate renewed theoretical work on core exciton models and electronic structure of nitrogen impurities in type-IA diamond.

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