Soft-X-Ray Resonant Inelastic Scattering at the C *K* Edge of Diamond

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We present carbon *K* emission spectra of diamond excited with high-resolution undulator radiation. The valence-band emission spectra are shown to be strongly dependent on the excitation energy, up to 20–30 eV above the C *K* edge. It is proposed that the dependence is indicative of the resonant inelastic scattering description of these emission spectra, i.e., the absorption-emission process should be described as a single scattering event where the momenta of the photoelectron and the valence hole in the final state are related by momentum conservation.

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X-ray absorption and the consequent decay through x-ray emission near an absorption edge are generally assumed to be two independent one-photon processes. With the exception of the x-ray resonant Raman scattering [1–3] and emission from molecules [4,5], there has been no clear experimental evidence questioning the validity of this assumption and thus no need to interpret this type of photon-in–photon-out experiment by the general x-ray inelastic scattering treatment [3]. Recent synchrotron radiation studies showing strong excitation energy dependencies in the x-ray emission spectra [5–10] were mostly attributed to multielectron processes such as shakeup satellites within the "absorption followed by emission" picture [11]; i.e., the absorption and emission processes are independent.

In this Letter we report carbon *K* emission spectra of diamond excited with high-resolution synchrotron radiation. The intensities of valence-band features are shown to be strongly dependent on the energy of the incident photons which excite the C 1*s* electrons into successive symmetry points in the conduction band, suggesting the presence of correlation between the absorption and emission processes. Furthermore it appears that this correlation can be related to the momentum of the photoelectron and that of the valence hole in the final state. We propose that the excitation energy dependence can be explained most straightforwardly by treating the absorption-emission process as a single inelastic scattering process with well-defined momentum conservation. In this interpretation, as a result of the negligible momentum transfer from the soft-x-ray photon, the final state of the solid prefers to have equal momentum for the photoelectron and the valence hole. This enhances emission from symmetry points where the photoelectron has been excited to. Since, with the availability of the next generation synchrotron radiation sources, emission experiments excited with high-resolution photons will be performed with increasing frequency, our results have important implications for interpreting these experiments. Finally, the use of the momentum-resolved inelastic scattering as a new band mapping technique will be discussed briefly.

Diamond was chosen for this study because it has a very simple and broad band structure that has been well studied. For this system of delocalized *sp* electrons, correlation effects, which have been found to be very important in the previously studied synchrotron-radiation-excited emission spectra of narrow band materials [4–9], are expected to be negligible. Indeed, the C *K* emission and absorption spectra were found to be absent of complicating satellite structure and well described by the calculated single-particle density of states based on the electronic band structure [12–14].

The experiment was performed at the beam line X1B of the National Synchrotron Light Source. The beam line, using the X1 undulator and spherical grating monochromator, provides intense high-resolution soft-x-ray radiation [15]. The C *K*-edge emission spectra were measured using a high-resolution grazing-incidence multigrating spectrometer with a two-dimensional detector [16]. The excitation bandpass was set to 0.3 eV at photon energies of about 300 eV. The emission spectra presented in this Letter were taken with the spectrometer resolution set to about 0.9 eV. Calibration of the photon energy in the emission spectra was done by the *L*-edge emission of Cr metal. The diamond sample used in this experiment is a type-IIb single crystal which had previously been polished in olive oil. The C *K*-edge absorption spectrum was measured by monitoring the photocurrent. The sample was oriented so that the incident photon is 70° from the surface normal to minimize the self-absorption effect.

The C *K* emission spectra for a selected number of incident photon beam energies, together with an absorption spectrum, are shown in Fig. 1. The absorption spectrum is normalized by the photocurrent signal from a clean gold mesh to correct for the carbon contamination of the

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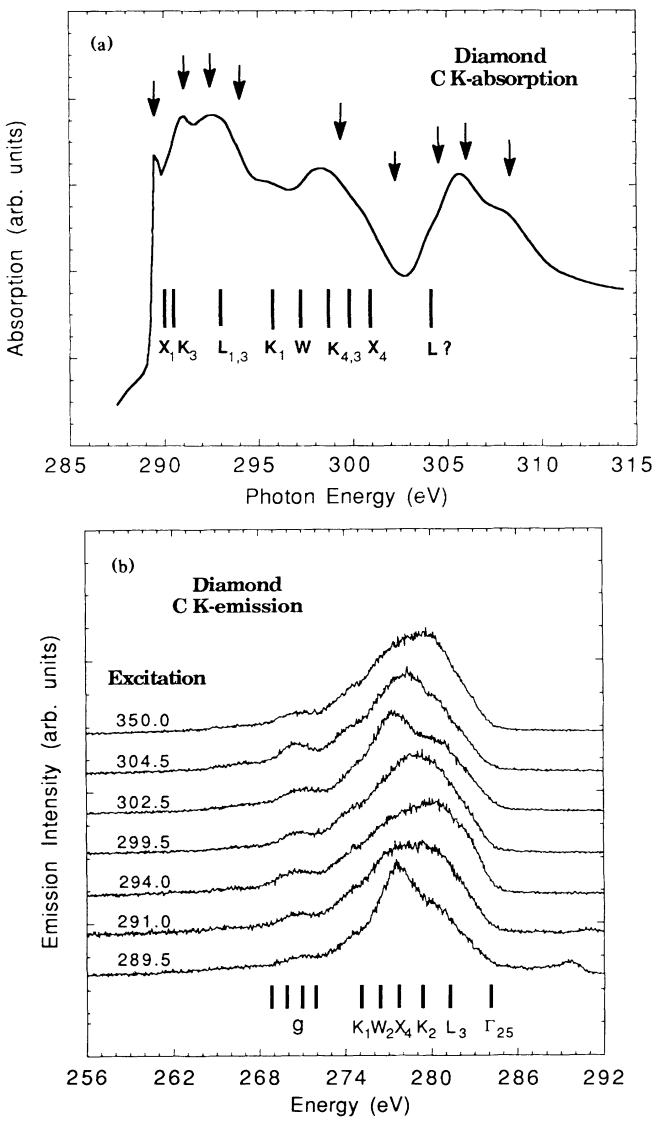

FIG. 1. C K-edge (a) absorption and (b) emission spectra of diamond. The emission spectra were taken at selected excitation energies indicated by the arrows in (a). Each spectrum has been normalized by its total area. The symmetry points are indicated by the vertical bars in both (a) and (b); g in (b) represents a group of symmetry points, K,X,W,L.

beam line optics. Note that the absorption and emission spectra measure the unoccupied and occupied p density of states, respectively, multiplied by the transition matrix elements. With the exception of the core exciton, the absorption and emission spectra compare favorably with the calculated density of states for diamond [12–14,17]. Thus, features in these spectra can be identified with the critical points in the band structure where the densities of states are large. The assignment of the critical points for both the absorption and the emission spectra, using results of Refs. [17–19], is also summarized in Table I and indicated in Figs. 1(a) and 1(b). The energies listed in

TABLE I. Measured and calculated energies at critical points for diamond. The calculated values are taken from Ref. [18] except as noted. All energies are in eV.

Photon	Relative to VBM	Calculation	Assignment
304.5 [a]	20.5	20 [c]	L
302.5 [a]	18.5	16.8	X_4
294.0 [a]	10.0	9.2/9.6	L_1,L_3
291.0 [a]	7.0	6.4 [d]	K_3
289.5 [a]	5.5	5.91	X_1
284.0 [b]	0	0	Γ_{25}
282.0 [b]	−2.0	−2.8	L_3'
279.5 [b]	−4.5	−5.2 [d]	K_2'
277.7 [b]	−6.3	−6.3	X_4
		−8.0 [d]	W_2
274.0 [b]	−10	−9.0 [d]	K_1
		−12 [d]	W_1
		−12.4	X_1
270.0 [b]	−14	−13.1	L_1
		−15.3	L_2'

[a]Photon excitation energy.
[b]Estimated from emission spectra in Fig. 1(b) with error bar of 0.5 eV (except 0.2 eV for the 277.7 eV case).
[c]Estimated from Ref. [17].
[d]Experimental result of Ref. [19].

the table are estimated relative to the top of the valence band. The peak at 289.5 eV in both Figs. 1(a) and 1(b) is due to the C 1s core exciton [12,14,20] and will be discussed elsewhere.

The valence-band spectra are strongly dependent on the excitation energy up to about 20–30 eV above the K edge. Careful inspection of these spectra suggests that this dependence is mostly in the intensity distribution among the valence-band features; i.e., the peak positions do not appear to change significantly. For example, the peak at 277.7 eV is very strong in the spectra excited with 289.5- and 302.5-eV photons, while weaker in other spectra. This suggests that the excitation energy dependence arises from variations in the transition matrix elements with the incident photon energy, rather than some dynamical process such as shakeup of a valence electron during either the absorption or the emission process.

The strong excitation energy dependence implies that the emission is dependent on the absorption process. It should be emphasized that valence-band emission has not been shown to depend on the excitation energy in narrow band solids, e.g., emission from solid Xe and Kr [9]. To our knowledge, the only observations of excitation energy dependence in the valence-band emission of solids were the L emission spectra of Si [8], and at the O K emission in the high-temperature superconductors [4]. Even though the dependence is tentatively attributed to electron correlation effects [8], the poor energy resolution used renders this interpretation inconclusive. Since satellites only accidentally overlap the valence emission bands it is unlikely that they cause the apparent spectral varia-

tions in the broad band materials. Hence we propose a new interpretation for our results that is more intuitive and straightforward.

Since our experiment is a two-photon process, the most general treatment is by the theory of x-ray inelastic scattering [3,11]. In this scattering picture, the initial state $|i\rangle$ of the solid is the ground state and the final state $|f\rangle$ has one electron in the conduction band and a hole in the valence band. The energy and the momentum are conserved in this scattering process. The energy loss by the incident photon is used to create the valence-hole–photoelectron pair. Momentum conservation dictates that the momentum of the electron-hole pair $(\mathbf{k}_c,\mathbf{k}_v)$ equals the momentum change of the incident $(\mathbf{q}_1)$ and emitted $(\mathbf{q}_2)$ photons: $\mathbf{k}_v+\mathbf{q}_1=\mathbf{k}_c+\mathbf{q}_2+\mathbf{G}$, where $\mathbf{G}$ is a reciprocal-lattice vector. These relations can be obtained from the Kramers-Heisenberg formula [11]:

$$\frac{d\sigma}{d\Omega}\propto\left|\sum_m \frac{\langle f|\mathbf{p}\cdot\mathbf{A}|m\rangle\langle m|\mathbf{p}\cdot\mathbf{A}|i\rangle}{E_m-E_i-\hbar\omega_1-i\Gamma/2}\right|^2, \tag{1}$$

where only the resonant term is kept. The intermediate state $|m\rangle$ is the core hole state with lifetime width Γ and the photoelectron in the conduction band. Using the single-particle picture with ε_{1s} and $\phi(\mathbf{r}-\mathbf{R})$ denoting the binding energy and the wave function of the C $1s$ electron located at lattice point $\mathbf{R}$, ε_c and the Bloch function $e^{i\mathbf{k}_c\cdot\mathbf{r}}u_1(\mathbf{r})$ for the conduction band state, ε_v and $e^{i\mathbf{k}_v\cdot\mathbf{r}}\times u_2(\mathbf{r})$ for the valence band, the scattering cross section can then be written as [21]

$$\frac{d\sigma}{d\Omega}\propto\left|\sum_{\mathbf{k}_c} M_{1s,v}\left(\frac{M_{c,1s}}{\varepsilon_{1s}-\varepsilon_c(\mathbf{k}_c)-\hbar\omega_1-i\Gamma/2}\right)\sum_{\mathbf{R}} e^{i\mathbf{R}\cdot(\mathbf{q}_1-\mathbf{q}_2+\mathbf{k}_v-\mathbf{k}_c)}\right|^2, \tag{2}$$

where the matrix element $M_{1s,v}=\int\phi\mathbf{p}\cdot\mathbf{e}u_2e^{-i\mathbf{r}\cdot(\mathbf{q}_2-\mathbf{k}_v)}\times d^3r$, etc. We also assumed no electron-phonon coupling; i.e., the matrix elements ε_{1s} and ε_c are independent of the position of the atom in the derivation. The last sum over all the atomic sites gives the momentum conservation. The energy of the scattered photon, $\hbar\omega_2=\hbar\omega_1-\varepsilon_v+\varepsilon_c$, can also be written as $[\hbar\omega_1-(\varepsilon_{1s}-\varepsilon_c)]+[\varepsilon_{1s}-\varepsilon_v]$. The first term is the denominator in the Kramers-Heisenberg formula. By tuning the incident photon energy so that the photoelectron is predominantly excited into a specific critical point in the conduction band, determined by $\hbar\omega_1=\varepsilon_{1s}-\varepsilon_c(\mathbf{k}_c)$, the absorption process selects a particular $\mathbf{k}_c$. Consequently, the emission occurs predominantly at $\mathbf{k}_v=\mathbf{k}_c+\mathbf{q}_2-\mathbf{q}_1+\mathbf{G}$ and $\hbar\omega_2=\varepsilon_{1s}-\varepsilon_v$. This picture provides a natural and straightforward explanation for the observed excitation energy dependence.

First of all, since the momentum of the soft-x-ray photon (the wavelength is of the order 40 Å) is very small compared to the size of the Brillouin zone of diamond, $\mathbf{q}_1$ and $\mathbf{q}_2$ can be neglected in comparison with $\mathbf{k}_v$ and $\mathbf{k}_c$. Thus there is no appreciable momentum transfer in the coherent scattering process: The momenta of the photoelectron and the valence hole should be equal. The most intense feature in the $\hbar\omega_{\rm ex}=289.5$ eV spectrum in Fig. 1(b) is near the symmetry point X_4, i.e., the filling of the core hole by a valence electron from around the X_4 point. As we see in Fig. 1(a) and the band structure of diamond [17,18], the photoelectron is promoted preferentially to the core exciton [12,14,20] as well as to the neighborhood of the X_1 point in the conduction band. Similarly, the 294-eV photon excites the photoelectron to near the L_1 and L_3 points, and a valence hole is created preferentially at the L_3' point to maintain momentum conservation. Indeed, we observed some enhancement in the emission spectrum in the region of L_3. At incident energies of 301 and 302.5 eV, the X_4 point is enhanced again due to the excitation to the region of the second band gap which is bordered by the X_4 point at the top of the conduction band. Since the accuracy of the band-structure calculation begins to deteriorate at higher energies, it may not be surprising to find some disagreement between our interpretation and the band theory. This discussion is more clearly illustrated in Fig. 2, where the difference spectra between the 350-eV spectrum and other spectra in Fig. 1(b) are shown to emphasize the excitation energy dependence.

Figure 2 also suggests that about 60% of the emission is independent of the excitation, which we tentatively call incoherent scattering. The origin of this contribution may be the following. (1) Since the absorption process excites the photoelectron also to other points in the Brillouin zone, through $\hbar\omega_1=\varepsilon_{1s}-\varepsilon_c(\mathbf{k})$ and the overlapping of different bands, emission due to these points also contributes to the emission spectra. (2) Many-body effects, such as electron-electron and electron-phonon interactions, may be important. For example, the scattering of the photoelectron before the emission and the dependencies of the matrix elements ε_{1s} and ε_c on the position of the atoms could destroy the momentum relations. Clearly, all these interactions must be taken into account in the calculation of the scattering cross section to reproduce the full experimental spectra. In summary, these cumulative pieces of evidence suggest that the inelastic scattering description of this photon-in–photon-out process offers a reasonable explanation for the excitation energy dependence in the emission spectra and provides the basis for further theoretical investigations.

Even though the scattering picture explains qualitatively our observations, we cannot rule out other explanations for the excitation energy dependence. As we discussed

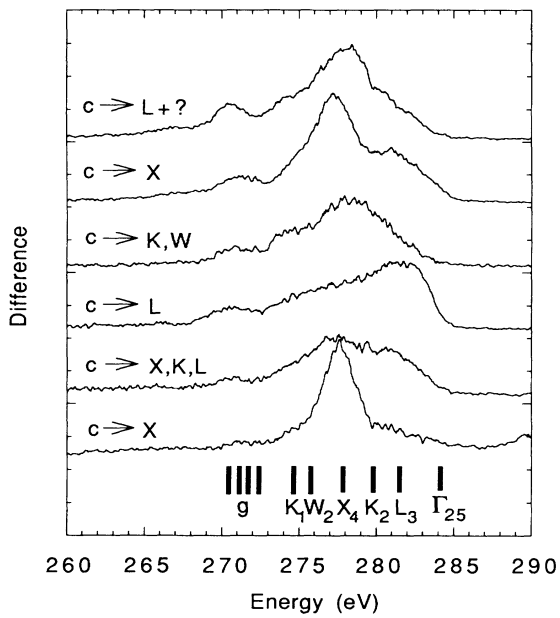

FIG. 2. Difference spectra: differences between the spectra in Fig. 1(b) and 60% of the 350-eV spectrum. The labels for each spectrum are used to indicate that the core excitation process, e.g., $c \rightarrow X$, indicates that the core electron is mostly excited to the X point in the conduction band. The bars at the bottom specify the decay of the valence electron to the core hole, e.g., X_4 indicates that the decay is from the X_4 symmetry point in the valence band. These spectra were slightly smoothed.

before, it is unlikely that the dependence is due to correlation satellites. However, it remains possible that the photoelectron could cause the observed spectral variations [8]. This would require that the photoelectron be localized near the core hole as a spectator electron, influencing the emission process through interaction with the valence electrons. However, the mechanism for the localization in this well-characterized, delocalized, *sp* system and the detailed interaction between the photoelectron and the valence band are not known. Furthermore, it is doubtful that this can be true at more than 20 eV above the edge. Thus without detailed calculation, it is not clear that this approach can explain the observed excitation energy dependence. In view of these arguments and the fact that the scattering approach provides a much more straightforward and intuitive explanation, we believe it to be the appropriate interpretation for our results.

Finally, we comment on the use of this momentum resolved scattering technique for the mapping of electronic bands. Since it is a photon-in–photon-out technique, it has several advantages for band mapping, such as bulk sensitivity, no sample charging problem, and the ability to work in external electric or magnetic fields. In addition, it has all the benefits of x-ray emission spectroscopy, i.e., probing the element specific and angular-momentum-resolved electronic states.

In summary, we have observed strong excitation energy dependence in the carbon K emission spectra of diamond. The dependence is believed to stem from the resonant inelastic scattering and related to the band structure of the diamond. This interpretation has important implications for all the emission experiments excited with high-resolution synchrotron radiation and points to the possible use of photon-in–photon-out technique for electronic band mapping.

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