

Brief Reports

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Band structure and x-ray resonant inelastic scattering

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We present the results of a tight-binding calculation of the soft-x-ray emission spectra obtained in an earlier study of resonant inelastic scattering of x rays at the carbon k edge of diamond. The close agreement between the calculated spectra and the experimental observations lends support to a picture of momentum conservation restricting the emission process to the same point in the Brillouin zone sampled by the initial excitation. We thus demonstrate qualitatively the feasibility of band-structure determinations with this technique.

X-ray absorption and emission spectroscopies have long been used to study the electronic properties of matter. However, the lack of momentum information has traditionally restricted these techniques to studies of the integrated densities of states (DOS) in the unoccupied and occupied electronic bands, respectively.¹ Information on the momentum-resolved electronic band structure has been obtained from the different photoelectron spectroscopies.² Recently it has been suggested that the excitation energy dependence observed in the resonant C k -edge soft-x-ray emission of diamond is evidence for an inelastic description of the adsorption-emission process.³ Momentum conservation between the photons and electrons involved in the excitation and decay restricts the radiative decay of the excited state to those regions of the Brillouin zone that are sampled in the initial photoexcitation. With this restriction, it has been suggested that x-ray resonant inelastic scattering (XRIS) may also be used to obtain momentum-resolved information on the electronic band structure. These ideas have been qualitatively discussed elsewhere.³ Experimental evidence providing further support for these ideas has also recently been provided by the observation that resonant emission at the L edge of amorphous Si differs markedly from the observations of L -edge emission in crystalline Si.^{4,5}

In this paper we investigate further the role of momentum conservation in XRIS by comparing the experimental observations with calculated valence-band densities of states for diamond. In particular, as in the model outlined above, we restrict the calculated valence-band densities of states to those regions of the Brillouin zone sampled by the initial excitation. In this way, we simulate

the momentum conservation and the resonant condition of the experiment. Described in greater detail below, the restricted DOS that we calculate show remarkable agreement in overall structure with the experimental observations.³ Indeed, our calculation indicates that the resonant process resulting in coherent emission represents a relatively large component, ~ 30 – 40 %, of the total emission as compared to the incoherent emission where the momentum information has been lost. We are thus able to show that the technique offers new access to momentum-resolved electronic-structure information. In particular, because the technique represents photon-in-photon-out, it offers the possibility of obtaining information on the electronic structure of insulators and polycrystalline samples. It is bulk sensitive and able to probe the electronic structure of buried interfaces.

We first review the XRIS formalism. An incident photon with energy $h\omega_1$ is tuned to an adsorption threshold, in the present case the C K edge of diamond, exciting an electron in the initial state $|i\rangle$ to the conduction band at some energy $\epsilon_c(\mathbf{k}_c)$. The radiative decay of this intermediate excited state $|m\rangle$ to a final state $|f\rangle$ involves the transition of a valence electron from a state at energy $\epsilon_v(\mathbf{k}_v)$ to the empty core state with the emission of a photon of energy $h\omega_2$. Within the framework of second-order perturbation theory, it is possible to show that the cross section for such resonant-scattering processes takes the form⁶

$$\frac{d\sigma}{d\Omega} \propto \left| \sum_m \frac{\langle f | \mathbf{A} \cdot \mathbf{p} | m \rangle \langle m | \mathbf{A} \cdot \mathbf{P} | i \rangle}{E_m - E_i - h\omega_1 - \Gamma_m / 2} \right|^2, \quad (1)$$

where E_m and Γ_m are the energy and lifetime of the state $|m\rangle$ and the sum is over all possible intermediate states. In the present case, taking a one-electron picture we describe the conduction and valence electrons by Bloch wave functions of the form $\phi_c = e^{i\mathbf{k}_c \cdot \mathbf{r}} u_c(\mathbf{r})$ and $\phi_v = e^{i\mathbf{k}_v \cdot \mathbf{r}} u_v(\mathbf{r})$. The vector potentials of the incoming and outgoing photons are represented by $\mathbf{A}_n = \boldsymbol{\varepsilon}^{(n)} e^{i\mathbf{q}_n \cdot \mathbf{r}}$ where $\boldsymbol{\varepsilon}^{(n)}$ is a linear polarization vector whose direction depends on the photon propagation vector \mathbf{q}_n . The cross section, Eq. (1) becomes^{3,7}

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

The core wave functions are localized at sites \mathbf{R} with the sum over all sites within the coherent length of the incident x ray. The individual matrix elements

$$M_{c,1s} = \int \phi_{1s} \mathbf{p} \cdot \boldsymbol{\varepsilon}_1 u_c d^3r, \quad (3)$$

$$M_{1s,v} = \int \phi_{1s} \mathbf{p} \cdot \boldsymbol{\varepsilon}_2 u_v d^3r$$

with ϕ_{1s} representing the core-level wave function describe the absorption and emission processes, respectively. They are used in the usual calculations of x-ray absorption and emission spectra. In the present study, with the bandwidth of the conduction and valence bands being small compared with the binding energy of the core levels involved, each matrix element is approximated by a constant. However, the matrix elements do introduce the dipole selection rules, and hence, determine the symmetry of the states that are sampled; if the core hole is s -like as in the case of the carbon K edge, only p -like conduction- and valence-band states are involved in the transitions.

Within the band structures of the solid, the resonant-absorption condition is $\varepsilon_c(\mathbf{k}_c) - \varepsilon_{1s} = \hbar\omega_1$, which determines the momentum of the excited electron. The energy of the emitted photon, $\hbar\omega_2 = \varepsilon_v(\mathbf{k}_v) - \varepsilon_{1s}$, results in an energy conservation for the complete inelastic process given by

$$\hbar\omega_2 = \hbar\omega_1 - \varepsilon_c + \varepsilon_v. \quad (4)$$

From Eq. (1), the momentum conservation is given by

$$\mathbf{k}_v = \mathbf{k}_c - \mathbf{q}_1 + \mathbf{q}_2 + \mathbf{G}, \quad (5)$$

where \mathbf{G} is a reciprocal lattice vector. This relation is the principal difference between the resonant inelastic scattering and the conventional picture of incoherent emission where the momentum information is lost. Thus, in the resonant process, if we neglect the photon wave vectors, which are small compared to the Brillouin-zone size at the C K edge, only the valence electrons with momentum given by $\mathbf{k}_v = \mathbf{k}_c + \mathbf{G}$ can decay into the core hole. *Changing the excitation energy will, therefore, change the emission spectral line shape. At higher photon energies, e.g., the Si K edge, the photon wave vector will not be small. Varying the detection angle \mathbf{q}_2 will make it*

possible to map the valence bands.

Based on the above discussion, we now proceed to calculate the C K emission spectra of diamond. With the matrix elements taken as constants, the absorption or emission spectra reflect the density of states of the conduction or valence bands, respectively. The principle of the calculation is illustrated in Fig. 1. For a fixed photon energy, we first locate the region of the Brillouin zone determined by the resonance condition, $\varepsilon_c(\mathbf{k}_c) - \varepsilon_{1s} = \hbar\omega_1$. This condition is satisfied within the horizontal lines in Fig. 1. The width ΔE of the strip represents the convolution of the core-hole lifetime broadening, the energy spread of the incident photons, and the lifetime width of the excited state, i.e., uncertainties in ε_{1s} , ε_c , and $\hbar\omega_1$, respectively. In the calculation, this finite width is modeled by a Gaussian function with a full width at half maxima of $\Delta E = 0.3$ eV. The total valence-band p -density of states is then calculated using only those regions of the Brillouin zone (BZ) that have conduction-band states falling within this finite width. In essence, the calculated spectrum $D(E, \hbar\omega_1)$ given by

$$D(E, \hbar\omega_1) \propto \sum_{c,v} \int_{\text{BZ}} d^3k \delta(E_{1s} - E_c - \hbar\omega_1) \times \delta(E_{1s} - E_v - E) \delta(\mathbf{k}_c - \mathbf{k}_v) \quad (6)$$

is just a joint density of states (JDOS), similar to that calculated for optical spectra, but restricted to the regions of the Brillouin zone determined by the resonant condition

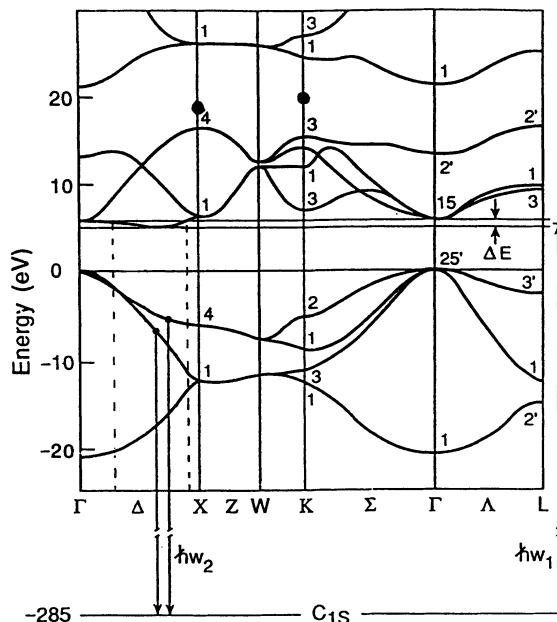


FIG. 1. The calculated band structure for diamond from Ref. 7. The incident photon exciting from the carbon $1s$ core level to the conduction band is indicated by $\hbar\omega_1$ and the photon involved in the radiative decay by $\hbar\omega_2$. The valence bands included in the radiative decay following excitation to a region of the conduction band are indicated by the vertical dashed lines. ΔE represents the energy spread in the initial excitation. The solid circles represent critical points determined in the present experiment.

and further restricted by the dipole selection rules. We will call this quantity the restricted joint density of states (r -JDOS). The spectrum obtained by this procedure is broadened further by a Gaussian of width 2 eV to include the effects of spectrometer resolution and the lifetime of the electron-hole pair in the final state. Finally, the spectra are weighted by an ω^3 dependence reflecting the frequency dependence of photon emission. Any dependence on the incident photon frequency is ignored as this merely introduces a scaling between spectra but not within a spectrum.

The energy bands of diamond are obtained from a tight-binding calculation using three center nonorthogonal parameters fitted to an empirical pseudopotential calculation.⁸ Using a basis set of four s and p orbitals, densities of states are obtained by using the standard method of calculating at selected points within the minimal wedge representing $\frac{1}{48}$ of the Brillouin zone. A comparison of the calculated bands with those obtained in pseudopotential calculations⁹ is reasonable up to approximately 10 eV above the middle of the band gap. Away from this energy range, the main deviation is a narrower bandwidth obtained in the tight-binding calculation; the conduction band being only 8 eV wide, as opposed to the 12–13-eV width estimated from experiments. The energy origin or the Fermi level is chosen as the top of the valence band, Γ_{25} .

In Fig. 2(a) we present a series of calculated r -JDOS. The excitation energies labeled in the figure are referred to the minimum of the conduction band. As expected, the r -JDOS at the different excitation energies are dramatically different, demonstrating the effect of the momentum-conservation restriction. With excitation to near the conduction-band minimum around the X point, the most intense peak in the JDOS is at 6.5 eV, contributed mostly from the region around X_4 in the valence band.

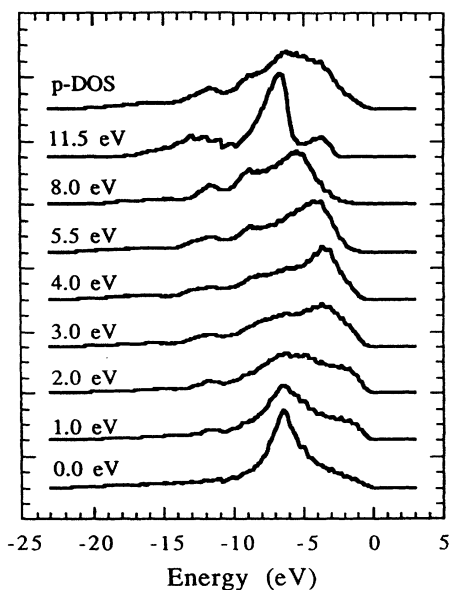


FIG. 2. Calculated photon emission spectra or r -JDOS as a function of the initial excitation energy measured with respect to the conduction-band minimum.

As the excitation energy is increased, contributions come into the r -JDOS from different regions in the Brillouin zone. As the excitation energy passes through the region 4.0 eV above the conduction-band minimum, the r -JDOS shows a peak derived from the L_3 near the top of the valence band. At higher excitation energies the photons sample the critical points in the region K , W , and then return again to the X point. In the middle of the conduction band it is possible to identify contributions to the calculated spectra from several regions in the Brillouin zone, a reflection of the overlapping bands, resulting in multiple solutions to the resonance condition. At high excitation energies corresponding to excitation to free-electron-like states, the electron momentum can take virtually any value due to folding of the different bands back into the first Brillouin zone. Thus, at high photon energies, the spectra will be free from the momentum-conservation restriction and will closely resemble the spectra obtained from electron excitation. The spectra in Fig. 2(a) closely resemble the experimental results of Ref. 3, which are reproduced in Fig. 3. The spectra shown in Fig. 3 have a component subtracted due to the incoherent emission. This latter component, approximately 60% of the total emission, is represented by the spectrum obtained for incident photons well above threshold or for incident electrons. In both cases the momentum information will be lost.

We now consider the possibility of critical-point determination. In Fig. 3, the spectrum excited with incident photon energy $h\omega_1 = 302.5$ eV, corresponding to a final state 13.0 eV above the conduction-band minimum, shows a well-defined peak representing emission from the X point in the valence band. This in turn suggests the presence of an X critical point at this final-state energy, as we have indicated in Fig. 1. The peak in the experimental emission spectrum at this critical point is shifted by 0.5 eV when compared to the spectrum corresponding to

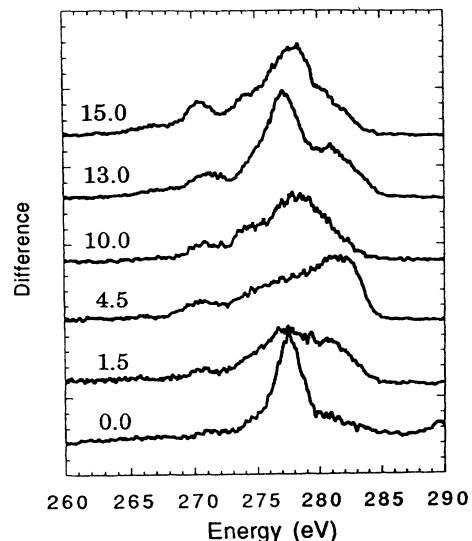


FIG. 3. Experimental observed photon emission spectra as a function of the initial excitation energy measured with respect to the conduction-band minimum.

excitation at the lower-incident photon energy of 289.5 eV. This observation is reproduced in the calculated r -JDOS. The shift is attributed to the fact that at the higher energy the conduction bands disperse rapidly away from the critical point as can be seen in Fig. 1. As another example, we consider the emission spectra resulting from excitation with incident photon energies $h\omega_1 = 299.5$ and 304.5 eV, corresponding to final states 10.0 and 15.0 eV above the Fermi level, respectively. Both show a small emission feature at 274 eV. We conclude, therefore, that for these incident photon energies the emission reflects excitation to the critical point of K symmetry, as we have also indicated in Fig. 1. These examples illustrate the use of the technique for critical-point determination.

The calculated spectra also reproduce many of the smaller features observed in the experimental spectra. If we consider the spectrum calculated for excitation up to an energy 11.5 eV above the conduction-band minimum, i.e., the X_4 point, we observe, as in the equivalent experimental spectrum, the main peak corresponding to emission from the X_4 point in the valence band and smaller peaks at -12.5 eV, corresponding to X_1 in the valence band, and at -3.5 eV from the L_3 point. The latter observation reflects the finite resolution in the incident photon beam leading to excitation to the L_2 point in the conduction band. We would also comment on the lack of any significant observation in the experiment of photon emission from the Γ point. The dipole selection rules will

allow emission only from the $\Gamma_{25'}$ close to the Fermi level. However, examination of the total valence band p -DOS, the top spectrum in Fig. 2(a), shows that the available density of states in this region is relatively low, a reflection of the dispersion of the relevant bands away from the Γ point. Indeed, the strongest features in the spectrum will reflect those bands with the smallest effective mass.

To summarize, therefore, we have shown through comparison of experiment with calculation that x-ray resonant inelastic scattering may be used as a means of obtaining band-structure information in systems that are not easily studied using the standard technique of photoemission. These might include insulating materials and polycrystalline samples or samples placed in electric or magnetic fields. Another possibility is that the presence of the core hole in the intermediate state will allow site-specific information to be obtained. The experimental resolution in the initial studies was of the order of 1 eV.³ However, with improved flux and resolution in the incident photon beam, it should be possible to achieve a total energy resolution comparable to the natural width of the C 1s lifetime width (0.1–0.2 eV).

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¹See, e.g., B. K. Agarwal, *X-ray Spectroscopy* (Springer-Verlag, Berlin, 1991).

²See, e.g., *Angle Resolved Photoemission*, edited by S. D. Kevan (Elsevier, Amsterdam, 1992).

³Y. Ma, N. Wassdahl, P. Skytt, J. Guo, J. Nordgren, P. D. Johnson, J.-E. Rubensson, T. Boske, W. Eberhardt, and S. D. Kevan, *Phys. Rev. Lett.* **69**, 2598 (1992).

⁴J.-E. Rubensson, D. Mueller, R. Shuker, D. L. Ederer, C. H. Zhang, J. Jia, and T. A. Calcott, *Phys. Rev. Lett.* **64**, 1047 (1990).

⁵K. E. Miyano, D. L. Ederer, T. A. Calcott, Y. Ma, J. C. Woicik, D. R. Mueller, W. L. O'Brien, J. J. Jian, L. Zhou, and Q.-Y. Dong (unpublished).

⁶See, J. J. Sakurai, *Advanced Quantum Mechanics* (Addison-Wesley, Reading, MA, 1967), Chap. 2.

⁷Y. Ma (unpublished).

⁸D. A. Papaconstantopoulos, *Handbook of the Band Structure of Elemental Solids* (Plenum, New York, 1986).

⁹G. S. Painter, D. E. Ellis, and A. R. Lubinsky, *Phys. Rev. B* **4**, 3610 (1971).