Bandstructure approach to near edge structure

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Summary

We review the current state of the art in EELS fingerprinting by computer simulation, focusing on the bandstructure approach to the problem. Currently calculations are made using a one electron theory, but we describe in principle the way to go beyond this to include final state effects. We include these effects within the one electron framework using the Slater transition state formula and assess the errors involved. Two examples are then given which illustrate the use of the one electron approximation within density functional theory. Our approach is to combine predicted bandstructure with predicted electronic structure to assist in fingerprinting of complex crystal structures.

An introduction to the formal theory

One electron picture

It has been known for some 25 years that extended fine structure can be understood from a simple, one electron quantum mechanical picture (Lee & Pendry, 1975). Experience over the last few years has shown, very surprisingly, that the near edge fine structure in EELS and XANES can also be predicted rather accurately using an independent electron quantum mechanical model. This means that we solve a one electron Schrödinger equation, such as

$$\frac{-\hbar^2}{2m} \nabla^2 + V_{\text{ext}}(\mathbf{r}) + V_{\text{xc}}(\mathbf{r}) \psi_i(\mathbf{r}) = \varepsilon_i \psi_i(\mathbf{r}), \quad (1)$$

usually in density functional theory, but possibly also in a simpler tight-binding model (Pettifor & Cottrell, 1992). Here, $V_{\text{ext}}(\mathbf{r}) + V_{\text{xc}}(\mathbf{r})$ is a local, one electron potential in that it depends only on a single electron coordinate, $\mathbf{r}$. The near edge structure can then be extracted using the eigenvalues $\varepsilon_i$ and eigenvectors $\psi_i$ by evaluating the relevant matrix element and calculating the quantity

$$\sum_{\mathbf{k}} |\langle \mathbf{n}\mathbf{k}|z|c \rangle|^2 \delta(\varepsilon - \varepsilon_{\mathbf{k}c}) \quad (2)$$

which, aside from a weak, logarithmic dependence on the characteristic scattering angle $\theta_0$ and the maximum scattering angle $\theta_{\text{max}}$ (Egerton, 1996), is proportional to the inelastic scattering intensity at an energy loss $E$ in the dipole approximation (Muller et al., 1998; Paxton et al., 2000). In Eq. (2), $|\mathbf{n}\mathbf{k}\rangle$ is the one electron state vector of an unoccupied band state of wavevector $\mathbf{k}$ and band index $n$ in the Brillouin zone and $|c\rangle$ is the state vector of the core level which is being excited. (Here $|\mathbf{n}\mathbf{k}|z|c\rangle = \int d\mathbf{r} \psi_{\mathbf{n}c}^*(\mathbf{r}) \psi_{\mathbf{k}z}(\mathbf{r})$, where $\mathbf{n}\mathbf{k}$ and $c$ represent the value of $i$ in Eq. (1) for the band state and core state respectively.) $z$ is one of the three directions in space. $\varepsilon_{\mathbf{k}c}$ is the band state eigenvalue and $\varepsilon$ is the energy, referred to the same zero of energy as $\varepsilon_{\mathbf{k}c}$, such that $E = \varepsilon - \varepsilon_{\mathbf{k}c}$, where $\varepsilon_{\mathbf{k}c}$ is the eigenvalue of the core level. Hence Eq. (2) is a sum over squared matrix elements of the transition from the core level to the band state at energy loss in question. The Dirac delta function, which picks out band states at the right energy, makes the sum look like a projected density of states† and one might try replacing the (squared) matrix element with a projector that ensures that the density of states is constructed from orbitals of the symmetry required by the selection rule. Hence for K-edges one might replace Eq. (2) with the $p$-projected local density of states. It turns out that this works very well in many cases.

In Eq. (1) $V_{\text{xc}}$ is the average electrostatic or Hartree potential seen by an electron, and $V_{\text{xc}}$ is the so called exchange and correlation potential, which in the local density approximation

$${\textstyle N(\varepsilon) = N(\varepsilon)}$$

†The density of states is defined as

and is regarded as a ‘fingerprint’ of the electronic structure in bandstructure theory.
(LDA), is computed at each point in space, \( \mathbf{r} \), as the exchange and correlation potential in a uniform electron gas having the density locally encountered at \( \mathbf{r} \).

This approximation has been shown over many years of experience to be an extremely good one for the calculation of ground state properties. Using the LDA we can predict equilibrium lattice and elastic constants, the stable crystal structure at 0 K and even approximate phase diagrams (e.g. Pettifor & Cottrell, 1992). Furthermore, as will be discussed below, the scheme is very reliable in molecular statics and dynamics to predict the structures of crystal defects. Moreover, the eigenvalues \( \epsilon_i \) and eigenvectors \( \psi_i \) in the Kohn–Sham Eq. (1) are strictly constructs of the theory and have no physical meaning. Nevertheless, the resulting values of \( \epsilon_{ak} \), or bandstructure, are frequently used to interpret experimental data, such as excitation energies measured by angle-resolved photoemission, giving quite good agreement with experiment in some cases (Desjonquères & Spanjaard, 1996).

Many electron effects

So it is curious that the local density approximation to the Kohn–Sham equations gives good agreement with experimental near edge structures. We view this in the following way (de Groot, 1991). The one electron picture focuses on the density of states of the ground state which is not observable. In any experiment designed to probe the electronic structure of a system with \( N \) valence electrons, one ends up with an excited state of the system having \( N + 1 \) (EELS or X-ray absorption) or \( N - 1 \) valence electrons (X-ray emission). In general we can say that the one electron picture is adequate if the density of states in the \( N + 1 \) or \( N - 1 \) electron systems is but little different from the \( N \) electron, ground state density of states. We then say that ‘final state’ effects are negligible. The natural way to go beyond the ground state theory was provided by Hedin in the 1960s who derived the following Schrödinger equation from the many body theory of interacting electrons (Hedin & Lundqvist, 1969):

\[
\left( -\frac{\hbar^2}{2m} \nabla^2 + V_{\text{ext}}(\mathbf{r}) \right) \psi_i(\mathbf{r}) + \int d\mathbf{r}' \Sigma(\mathbf{r}, \mathbf{r}'; E_i) \psi_i(\mathbf{r}') = E_i \psi_i(\mathbf{r}).
\]

Comparing with Eq. (1) the essential difference is that the local exchange and correlation potential has been replaced by a non-local, energy-dependent self energy operator, \( \Sigma \). Unlike in the density functional theory one can write down an explicit expression for the self energy \( \Sigma(\mathbf{r}, \mathbf{r'}; E_i) \) as a series expansion. Neglecting vertex corrections one obtains the so-called GW approximation (Ariasetiawan & Gunnarsson, 1998). In Hedin’s formalism, and its GW approximation, the energies \( E_i \) are actual excitation energies of the \( N + 1 \) or \( N - 1 \) valence electron systems; \( \psi_i \) are called quasiparticle wavefunctions. In fact \( E_i \) are complex numbers. The real part of the relevant \( E_i \) is the energy difference between the excited and ground states, and \( \hbar/\text{Im} \ E_i \) is the lifetime of the excitation. We can say that in EELS or XAS the energy loss measures the quasiparticle energy

\[
\text{Re} \ E_i = E_{\text{tot}}(N + 1, i) - E_{\text{tot}}(N). \tag{3}
\]

Here \( E_{\text{tot}}(N) \) is the ground state energy of the \( N \) electron system. \( E_{\text{tot}}(N + 1, i) \) is the total energy of the \( N + 1 \) electron system where the core electron has been promoted into an unoccupied valence state. We assume that the electrons have fully relaxed to screen the excitation, labelled \( i \); that is, we make the adiabatic approximation which amounts to saying that the scattering event is slow in the sense that the scatterer fully relaxes to equilibrium (Woodruff & Delchar, 1994). In the Hedin or GW approach, one must calculate the eigenvalues in Eq. (3) and put them into an equation similar to Eq. (2) in place of the \( \epsilon_{ak} \) with appropriate oscillator strengths calculated from the quasiparticle wavefunctions in place of the one electron matrix elements.

Transition state theory

Now let us describe a scheme that is part way between one electron and many electron approaches. Consider the cartoon in Fig. 1. Suppose we want to calculate the energy loss at the excitation edge for the core level illustrated. In a one electron picture, we imagine solving Eq. (1) and finding the eigenvalues of the core level and the lowest unoccupied state.‡ Then in this simple picture, the threshold energy loss will be the energy difference shown, namely \( E_i - \epsilon_i \). But the correct expression for the threshold energy is obtained by rewriting Eq. (3) as

\[
E_{\text{th}} = E_{\text{tot}}(q_i |_{q_i = 1}) - E_{\text{tot}}(q_i |_{q_i = 2}) \tag{4}
\]

that is, the total energy difference between the excited state with just one electron in the core and one extra electron at the Fermi level, and the ground state with two electrons in the core. This has been called ΔSCF by Slater as it is the energy difference between two self consistent fields. Here, \( q_i \) denotes the core charge in units of the electronic charge, and we express \( E_{\text{int}} \) as a continuous function of the core level occupancy, \( q_i \), which is regarded as a continuous variable (Janak, 1978).

Equation (4) is also correct in the density functional theory as long the excited state is the lowest energy state of that symmetry. (To that limited extent, density functional theory is able to describe an excited state. Beyond that one makes an approximation that the excited state can be correctly rendered in

‡In a metal, this is the Fermi level, \( E_F \); we could also extend the argument to consider excitations into some higher energy unoccupied state.

So we can try and find $E_{\text{th}}$ by calculating the two total energies. To do this we make two density functional calculations; one the ground state total energy, and another in which we constrain the core level to have just one electron, putting an extra electron in the lowest unoccupied band state. We will still make the local density approximation, but we are going beyond the one electron picture in the sense that we are not deducing $E_{\text{th}}$ from an eigenvalue difference. Instead ‘final state’ effects are included because in the second calculation the electron system responds self-consistently to the presence of the core hole. In metals this is done by screening and is a very localized effect; we find that the perturbation is limited to the atom on which there is a core hole and the screening is achieved by the valence orbitals on that atom. In insulators the perturbation is rather more long ranged and the effect of the core hole extends to a number of neighbour shells (Elsässer & Köstlmeier, 2001).

Recently, we calculated the anion K-edge threshold energy for 12 carbides and nitrides of Ti, V, Cr, Zr, Nb and Hf and compared them with experiment. We made the following conclusions (Paxton et al., 2000):

1 The one electron difference between ground state eigenvalues as in Fig. 1 is in error with respect to experiment by between $-19$ and $-23$ eV, i.e., large and negative. This is typical of the LDA, that the core levels are too weakly bound to the nucleus.

2 Comparison between direct evaluation of Eq. (4) and the transition state approximation shows agreement to within better than 0.5 eV. This shows that the ansatz in Eq. (7) is a good one.

3 The mean error between the transition state theory and experiment is $+4.22 \pm 0.44$ eV. This is an indication of the error made by the local density approximation in describing the screening of the core hole.
It is important to emphasize that the LDA error in eigenvalues is very large, but this is not a failure of the LDA itself, rather one should not attempt to identify the Kohn–Sham eigenvalues \( \varepsilon_i \) as excitation energies. Used properly, the LDA predicts the threshold energy to within about 4 eV with a rather uniform overbinding to the nucleus. In similar calculations, it has been shown that the GW approximation does a good job of correcting the LDA error. In fact it slightly overcompensates and the excitation energy is underestimated by about 1 eV (Arias et al., 1996).

We may remark parenthetically that Eqs (5), (6) and (7) imply that the quantity \( U_c \) is given by

\[
U_c = \frac{\partial^2 E_{\text{tot}}}{\partial q^2}.
\]

This is the curvature of the energy versus occupancy, sometimes called the ‘chemical hardness’ or ‘Hubbard–U’, in this case of the core state. It describes the energy penalty in adding or removing electrons from a state; for an atom it relates to the ionization energy and electron affinity (Parr & Yang, 1989). It has the units of a potential and although there is no such potential in the local density Hamiltonian (Anisimov et al., 1991), nevertheless it is calculated implicitly in the self consistent field. In fact, as we have seen, the screening of the core hole as described by \( U_c \) is fairly well predicted in the \( \Delta \text{SCF} \) employing the LDA.

Having made these introductory remarks, in the rest of this paper we will present the results of studies of two solid-state systems using the local density approximation to calculate near edge structure. Extensions to the GW approximation will become valuable in the future for dealing with, for example, the highly correlated Mott–Hubbard and charge transfer oxides such as NiO, CoO and the oxides of Cu, as well as important new materials such as high \( T_c \) superconducting cuprates and CMR manganates. But we repeat these are studies for the future.

We should also point out that our experience is that calculated near edge structure has an uncertainty of about 1 eV in relative peak positions and about 4 eV in absolute edge threshold energies. With the newer advances in instrumentation we are seeing experimental energy resolution as small as 0.1 eV. It therefore remains a challenge to the theory to find out whether this can be met within the local density approximation or using many body methods such as GW. Of equal importance to the calculation of accurate spectra given a set of atom positions in the solid state is the determination of these atom positions themselves. This point is illustrated in what follows, and it must not be forgotten that disagreement with experiment is just as likely to be due to uncertainty in atomic structure as uncertainty in electronic structure.

### Examples of the application of density functional theory

We present here two case studies of the density functional method applied to complex solid-state crystal phases. In the first case we review briefly an extensive piece of work on non-stoichiometric zirconia. In the second we show some previously unpublished results concerning the carbonitride \( \text{C}_3\text{N}_4 \). A complete description of our methodology has been published earlier in our work on transition metal carbides and nitrides (Paxton et al., 2000). The point we wish to make is that density functional theory in the local density approximation provides a powerful combination of capabilities. In the first instance the method is used in the calculation of interatomic forces which are used to find the lowest energy atomic structure of complex materials. Once the local structure of a defect or the equilibrium structure of a complex crystal is found, the same approach is used to extract from the self consistent electronic structure the near edge structure that would be expected in a fingerprinting experiment. Since, in the experiment, the electron or X-ray beam interacts with a certain volume of material, care must be taken to compute a weighted sum from each atom, suitably energy shifted relative to the core level calculated at that site; this is usually called the chemical shift and in the cases studied here it is only on the order of one or two electron volts. Its physical origin is the varying Madelung potential, \( V_{\text{cr}} \), encountered at crystallographically inequivalent sites.

#### Fingerprinting binary zirconia–yttria ceramics

Zirconia is a valuable ceramic material having both structural and functional roles. As a pure material it is of little use, because it undergoes two phase transformations, cubic to tetragonal to monoclinic as it is cooled from high temperature. The tetragonal to monoclinic transformation is accompanied by about a 4% volume increase. This can be exploited in a controlled way in transformation toughening (Richerson, 1992), but at the same time renders the pure material nearly impossible to process. Both in the control of toughening and for processability, zirconia is used alloyed with aliovalent oxides such as yttria. Introducing trivalent cations requires an accompanying concentration of charge compensating vacancies, and these vacancies serve to stabilize the cubic and tetragonal phases (depending on yttria concentration) in a way that has recently become rather well understood (Fabris et al., 2001, 2002). In this state, zirconia is said to be stabilized and the detailed disposition of the minority cations and the oxygen vacancies make for a complex crystal structure.

Our aim here is briefly to summarize our work that was aimed at obtaining fingerprinting detail at the oxygen K-edge in stabilized zirconia. A complete account of the work is already in print (Vlachos et al., 2001; Ostanin et al., 2001, 2002; McCombs et al., 2002).

In the present calculations, in view of the large unit cells and number of inequivalent sites, we have used just a local density of states of \( p \)-symmetry projected onto the oxygen anions to model the K-edge. We have not attempted an absolute estimate of the energy loss but have lined up the spectra to

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give the closest match with experiment. Chemical shifts are included, however. In Fig. 2 we show the calculated oxygen K-edge spectra in pure cubic, tetragonal and monoclinic zirconia. These are compared with experimental EELS spectra and it is clear that the agreement deteriorates going from monoclinic to tetragonal to cubic. The reason for this is that the monoclinic is a pure phase, but the others are stabilized by alloying. Clearly the next step is to attempt to model the structure of the stabilized zirconia. We did this by building large computational periodic unit cells of zirconia containing 96 atomic sites with the intention of mimicking 3, 5 and 10 mol%Y2O3–ZrO2 by the inclusion of the appropriate numbers of yttrium atoms and oxygen vacancies. Clearly there is a very large number of ways to construct such cells and the task is to find the most energetically stable arrangement by extensive molecular statics relaxations using the local density approximation in density functional theory. Having done this, we could extract the predicted EELS intensities as for the pure phases, using appropriate weighted sums and applying chemical shifts to average over the unit cell. The results are shown in Fig. 3. Full agreement is still not achieved but the filling in of the valley between the first two peaks is largely improved over the model employing pure phases. One possible cause of the remaining disagreement lies in our belief that the oxygen ions in zirconia lie in a rather flat, anharmonic potential energy well. Therefore at finite temperatures there will be large-amplitude phonon displacements that may further serve to fill in the intensity between the two peaks. Alternatively, we must either seek to improve our atomic models with larger unit cells or investigate the error from the local density approximation itself.

The crystal structure of C3N4

It was proposed some years ago that if C3N4 could be produced in the structure of β-Si3N4 this material would be harder than diamond (Liu & Cohen, 1990). This assertion has later been subject to some scrutiny, especially by Teter (1998), who pointed out that the original postulate was based on the predicted bulk modulus of β-C3N4 rather than its shear moduli, which are more likely to correlate with the hardness. Therefore it seems that we will have rather longer to wait than anticipated before diamond is superseded as the hardest material known.

However, the original suggestion led to at least two attempts to produce β-C3N4 by various techniques and then attempt to determine its crystal coordinates (Yu et al., 1994; Chowdhury et al., 1999). Whereas some electron diffraction patterns were produced, no EELS spectra have been reported. Our intention here is two-fold, firstly to propose that β-C3N4 has a less negative formation energy than α-C3N4 (C3N4 in the structure of α-Si3N4) and secondly to predict the crystal structure and EELS fingerprint of α-C3N4. This is another nice example of how the density functional theory in the local density approximation can be used in a combination of atomic structure and electronic structure prediction. Figure 4 shows a projection of the crystal structure of the two phases. We have minimized the self consistent total energy with respect to the lattice parameters of α-C3N4 and β-C3N4 with the results shown in Tables 1 and 2 and Fig. 5.
Our implementation of the density functional method uses a basis of linear muffin-tin orbitals (Methfessel et al., 2000) and our results compare very well with those of Liu & Wentzovitch (1994) who used a plane wave basis in a pseudo-potential method. This encourages us to believe that our results for $\alpha$-C$_3$N$_4$ are also correct and it is surprising that this modification is stable with respect to $\beta$-C$_3$N$_4$ by as much as 115 kJ g-mol$^{-1}$, see Fig. 5. This is roughly 100 times larger than typical energy differences between competing phases in carbon or silicon. We therefore regard it as extremely unlikely that C$_3$N$_4$ can be produced in its metastable $\beta$ phase. The $\alpha$-C$_3$N$_4$ crystal unit cell contains 28 atoms in six inequivalent positions (see Table 2). This is a fairly complex unit cell and as far as we are aware this is the first time that an attempt has been made to predict its structure. Having done that, and armed also with the calculated structure of $\beta$-C$_3$N$_4$, we can re-evaluate the electron diffraction patterns of the putative $\beta$-C$_3$N$_4$ phase by calculating structure factors from the calculated atomic structures. We have compared calculated and measured ring diffraction patterns in Fig. 6. Briefly, the differences between the two experimental sets of data are much larger than the predicted differences between $\alpha$-C$_3$N$_4$ and $\beta$-C$_3$N$_4$. We should point out that the experimental lattice parameters given in Table 1 are based on a fitting of the diffraction rings to the $\beta$-C$_3$N$_4$ structure by Yu et al. These are not inconsistent with an identification of the structure as $\alpha$-C$_3$N$_4$. However, it is significant that the calculated lattice constant, $a$, is larger than that measured, especially in view of

Table 1. Lattice parameters of $\beta$-C$_3$N$_4$. The space group is P6$_3$/m; there are 14 atoms per unit cell: 6 carbon and 6 nitrogen in Wyckoff position 6h and 2 nitrogen in 2c. The table shows the calculated lattice constant and axial ratio and the two internal coordinates of the 6h carbon and nitrogen positions. These are compared to earlier calculations by Liu & Wentzovitch (LW). There has been some experimental confirmation of these data; however, we contend here that this structure is metastable and unlikely to be observed.

<table>
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<th>Present work</th>
<th>LW</th>
<th>expt.</th>
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<td>Lattice constant (Å)</td>
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<td>6.41</td>
<td>6.30</td>
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<tr>
<td>Axial ratio</td>
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<td>0.375</td>
<td>0.378</td>
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<tr>
<td>Bulk modulus (GPa)</td>
<td>435</td>
<td>437</td>
<td></td>
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<tr>
<td>Cohesive energy (Ry/C$_3$N$_4$)</td>
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<td>3.51</td>
<td></td>
</tr>
<tr>
<td>Carbon (6h) x</td>
<td>0.177</td>
<td>0.178</td>
<td></td>
</tr>
<tr>
<td>Carbon (6h) y</td>
<td>0.771</td>
<td>0.772</td>
<td></td>
</tr>
<tr>
<td>Nitrogen (6h) x</td>
<td>0.331</td>
<td>0.331</td>
<td></td>
</tr>
<tr>
<td>Nitrogen (6h) y</td>
<td>0.031</td>
<td>0.033</td>
<td></td>
</tr>
</tbody>
</table>

Table 2. Lattice parameters of $\alpha$-C$_3$N$_4$ in the hexagonal setting. The space group is P31c; there are 28 atoms per unit cell: 12 carbon, $C_1$ and $C_2$, and 12 nitrogen, $N_1$ and $N_2$, in four inequivalent positions in 6c; two nitrogen, $N_3$, in 2a and two nitrogen, $N_4$, in 2b. The table shows the calculated lattice constant, axial ratio, bulk modulus, cohesive energy and the internal coordinates. In parentheses are the coordinates of an `ideal' $\alpha$-C$_3$N$_4$.}

<table>
<thead>
<tr>
<th>Lattice constant (Å)</th>
<th>Axial ratio</th>
<th>Bulk modulus (GPa)</th>
<th>Cohesive energy (Ry/C$_3$N$_4$)</th>
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<tr>
<td>6.43</td>
<td>0.720</td>
<td>434</td>
<td>3.18</td>
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<table>
<thead>
<tr>
<th>Internal coordinates</th>
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<tr>
<td>$x(C_1) = 0.516 (1/2)$</td>
</tr>
<tr>
<td>$x(C_2) = 0.159 (1/6)$</td>
</tr>
<tr>
<td>$x(N_1) = 0.353 (1/3)$</td>
</tr>
<tr>
<td>$x(N_2) = 0.314 (1/3)$</td>
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<td></td>
</tr>
</tbody>
</table>
the fact that the local density approximation consistently underestimates lattice constants.

The EELS near K-edge structure has been calculated from Eq. (2) after evaluating the matrix elements between band states and the 1s core electron. Our calculated spectra are displayed in Fig. 7. We have used the Slater transition state method described above to predict the energy loss at threshold and for consistency we have calculated the EELS near edge structure at each site while maintaining half a core hole at that site. The spectra are then weighted by the number of atoms per unit cell in each inequivalent site shifted by the chemical shift and summed. A spectrum is produced for each of the three cartesian directions $x$, $y$ and $z$ in the hexagonal setting of the $\alpha$- and $\beta$-C$_3$N$_4$. These are the $[\bar{2}1\bar{1}0]$, $[01\bar{1}0]$ and $[0001]$ Miller–Bravais directions. An EELS spectrum taken from a powder or polycrystalline specimen such as employed in the diffraction studies would amount to an average of these three; clearly the anisotropy of the crystal structure admits much additional structure for fingerprinting if a single crystal of known orientation were available.

Finally, we may speculate upon why $\beta$-C$_3$N$_4$ is apparently metastable with respect to $\alpha$-C$_3$N$_4$, and what are the structures that were manufactured in the experiments. Certainly, as we have remarked, the energy difference between the two crystal modifications is very large; on the other hand, bond lengths and angles in the first neighbour shells are rather different compared to, say, those between cubic and hexagonal diamond. But bear in mind that diamond and graphite are almost degenerate in energy while the bonding is radically different in the two phases. C$_3$N$_4$ is essentially a network of three-fold coordinated nitrogen atoms with bond angles near 120° covalently bonded to four-fold coordinated carbon atoms with bond angles near 109.47°. All first neighbour bonds are C–N bonds. In the very simplest picture of the internal energy at 0 K this will depend quadratically on the deviation from the mean bond length and the deviations from the 120° or 109.47° bond angles. Table 3 compares these in our relaxed $\beta$-C$_3$N$_4$ and $\alpha$-C$_3$N$_4$, and an ‘ideal’ $\alpha$-C$_3$N$_4$ whose atom coordinates are shown in parentheses in Table 2. This latter structure is special in that it has just two bond lengths, differing
however by a large ~8%, and a rather regular arrangement of bond angles. (It is not, of course, a higher symmetry phase.) The table shows rather clearly that the origin of the stability of $\alpha$-C$_3$N$_4$ over $\beta$-C$_3$N$_4$ is the smaller deviation in the nitrogen 120° bond angles. A closer look, in fact, shows that the nitrogen bonds in $\beta$-C$_3$N$_4$ are planar whereas those in $\alpha$-C$_3$N$_4$ are distorted out of plane. However, the nitrogens in 6h in $\beta$-C$_3$N$_4$ while planar have bond angles of 111.5°, 124.1° and 124.1° which are thereby rather distorted in the plane. Essentially the C$_3$N$_4$ structure is dominated by the Hume-Rothery ‘8-N’ rule (Pettifor, 1995) whereby the carbon is four-fold and the nitrogen three-fold coordinated. However, as we know, carbon is almost equally stable in the sp$^3$ diamond as the sp$^2$ graphite structure; that is, the bonding rather readily rehybridizes. This can be seen from the smaller s−p splitting of 8.6 eV compared to nitrogen’s 11.6 eV (Harrison, 1980). We therefore expect the carbon bond angles to be more flexible than the nitrogen bond angles. Hence, given that the bond length fluctuations are very small in both $\alpha$-C$_3$N$_4$ and $\beta$-C$_3$N$_4$ we expect the energetics to be dominated by the bond angle distribution. The carbon 109.47° angles are more widely distributed in $\alpha$-C$_3$N$_4$, but this entails less of an energy penalty than the deviations in the nitrogen 120° angles which are significantly less in the relaxed $\alpha$-C$_3$N$_4$ phase. Note the importance of properly relaxing the structures before making these comparisons. Simply using the parameters from Si$_3$N$_4$ or the ‘ideal’ $\alpha$-C$_3$N$_4$ in Table 3 would be misleading. Carbon is rather special compared to silicon in its ability to rehybridize and sustain quite large bond angle fluctuations as is evident from the very large number of metastable phases in pure carbon (Bokros, 1977). Note that the s−p splitting in silicon is 7.0 eV which apparently invalidates our argument. However, the first row elements are not comparable with other rows because of their ‘soft,’ 1s electron core (Pettifor, 1995). The
reason we expect the nitrogen atom to prefer the three-fold, 120° coordination is that the bonding in C\textsubscript{3}N\textsubscript{4} is expected to be more covalent than in boron nitride, or indeed ammonia or the ammonium ion. The bond angle in ammonia is 107° and in ammonium 109.47°, reflecting the increasing ionic character. BN has a metastable cubic, zincblende form with four-fold coordination, again presumably due to increased ionicity reflecting the large electronegativity difference compared to C\textsubscript{3}N\textsubscript{4}. However, the stable phase of BN is hexagonal with nitrogen in planar three-fold coordination as in C\textsubscript{3}N\textsubscript{4}.

We can therefore be clear that β-C\textsubscript{3}N\textsubscript{4} is highly metastable with respect to α-C\textsubscript{3}N\textsubscript{4}. It remains to ask what were the thin film structures observed in the experiments? The differences in the ring patterns between the two experiments are larger than between the theoretical α-C\textsubscript{3}N\textsubscript{4} and β-C\textsubscript{3}N\textsubscript{4} ring patterns. The microstructure is clearly complex and probably not the same in the two films. Quite possibly the films contained some third phase not considered here, or some more complex stacking of layers of α-C\textsubscript{3}N\textsubscript{4} and β-C\textsubscript{3}N\textsubscript{4} stabilized by growth on the substrate. However, there is no real evidence that the films had the [0001] texture that this would imply (Fig. 6). Unfortunately, no tilting experiments were made. In both experiments, contamination from the Si substrate was looked for and not detected; however, Yu et al. found 5–10% oxygen in their films. There is the possibility that metastable or distorted structures were stabilized by epitaxial strain although this would have to be very large to impose a noticable change in lattice constant. We cannot at present account for the discrepancy in lattice constant between the experiment and the theory.

**Discussion and conclusions**

We have tried to emphasize here the value of the density functional theory in making a combined calculation of atomic and electronic structure. Having computed the equilibrium (0 K) structure of phases that are under study in the microscope, we can predict near K-edge structure with an apparent reliability of about 1 eV in relative peak positions. The method is certainly sensitive to perturbations in the near edge structure due to dopants in stabilized zirconia. The question of the C\textsubscript{3}N\textsubscript{4} phases observed highlights the sensitivity of EELS over electron diffraction in this case. Figure 6 shows that if the C\textsubscript{3}N\textsubscript{4} were textured in [0001], then the electron ring patterns of α-C\textsubscript{3}N\textsubscript{4} and β-C\textsubscript{3}N\textsubscript{4} would be indistinguishable. However, while similar, there are sufficient differences in the near edge structure for the two phases to be resolved. In particular, we would expect to see three peaks at the carbon K-edge in polycrystalline β-C\textsubscript{3}N\textsubscript{4} in contrast to a single broad peak in α-C\textsubscript{3}N\textsubscript{4}. We are certain that the identification made by the authors of their films as β-C\textsubscript{3}N\textsubscript{4} cannot be supported in the light of our total energy calculations. Furthermore, our comparisons show that the indexing is no more consistent with β-C\textsubscript{3}N\textsubscript{4} than with α-C\textsubscript{3}N\textsubscript{4}. Further experiments will be needed and it is very clear that EELS will be a more sensitive tool than electron diffraction especially in the absence of orientated single crystals.

**References**


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