TiC and NbC

The soft x-ray emission spectra of several of the refractory metal carbides and related compounds have been studied extensively [21-26] and have received a wide variety of explanations and interpretations. The intent of the present section is to demonstrate that an approximate calculation of the lineshapes based on self-consistent APW energy-band calculations for these materials can yield unnormalized curves in good agreement with the experimentally observed spectra.

The calculation involves several fundamental approximations which are relatively commonly used [21-28] but warrant further investigation: (1) The localized nature of the initial state is ignored. It is assumed that the energy dependence of the transition matrix element should be well approximated by that matrix element calculated between the crystalline core and valence-band wave functions. (2) The distortion of the valence wave functions, and the resulting energy shifts, which are caused by the absence of a core electron in the initial state, are ignored. It is assumed that the effect on the matrix elements will be small and that, although the effect on the total energy is significant, the effect on energy differences between transitions from different parts of the valence band is negligible. (3) The variation of the vector potential $\underset{\sim}{A}$ over the dimensions

of the core wave function is ignored in order to reduce the calculation of $\langle \underset{\sim}{p}.\underset{\sim}{A} \rangle$ to the calculation of $\langle \underset{\sim}{p} \rangle$. This approximation is equivalent to ignoring the atomic form factors for these x-ray transitions and should certainly be adequate for the computation of the desired lineshape estimates.

With these approximations, the matrix element of $\underset{\sim}{p}.\underset{\sim}{A}$ between the initial and final states is reduced to the matrix element of $\underset{\sim}{p}$ between the one-electron core wave function and the valence wave function for a state at the desired initial energy. The expansion (inside sphere t),

$$\Psi_j(\underset{\sim}{k},\underset{\sim}{r}) = \sum_{\ell,m} C^t_{\ell,m}(j,\underset{\sim}{k})\, Y_\ell{}^m(\theta,\phi)\, R_\ell\, (E_j(\underset{\sim}{k}),r) ,$$

for an APW eigenfunction [2,4] of band j and wave vector $\underset{\sim}{k}$ then allows the usual atomic selection rules to be utilized to reduce the summations over ℓ and m. (In the expansion, $Y_\ell{}^m$ is a spherical harmonic, R_ℓ a radial function.) Examination of the radial functions R_ℓ for the materials of interest shows that their energy dependence, over the range of valence-band energies, is negligible. Furthermore, for these materials, a single value of ℓ dominates for each x-ray transition. The fractional variation in the frequency of x-rays emitted by valence electrons, as they drop into a given core level, is also negligible. Thus, the energy dependence of the x-ray intensity density is well