

## Final-state effects in carbon Auger spectra of transition-metal carbides\*

M. A. Smith<sup>†</sup> and L. L. Levenson

*Department of Physics and Graduate Center for Materials Research, University of Missouri-Rolla, Rolla, Missouri 65401*

(Received 11 February 1977)

The carbon Auger spectra of TiC, VC, and Cr<sub>3</sub>C<sub>2</sub> are measured with a resolution of 1.2 eV. Background subtraction is performed and a deconvolution technique is used to remove energy-dependent broadening from the spectra. An analysis of the data in terms of density-of-states calculations, x-ray emission work, and x-ray photoelectron data shows that final-state effects dominate the Auger spectra. For all of the carbides three peaks are identified as spectral terms resulting directly from final-state hole interactions. Other peaks appearing in the Auger spectra can be identified without final-state considerations.

### INTRODUCTION

In recent years, Auger transitions involving valence-band energy levels have been investigated in an attempt to obtain chemical information about solid surfaces. Studies of some of these transitions have been attempted in response to a suggestion by Lander<sup>1</sup> that Auger spectra of the type *XVV* (*X* designates the initial hole state and *V* designates a valence state) should be the self-convolution of a function involving the valence-band density of states. Studies of this type have been done for silicon<sup>2</sup> and graphite.<sup>3,4</sup> Studies of a different kind, however, have received much more attention. These investigations have examined the spectra of elements showing "chemical effects" or changes in peak shape and energy upon combination with another element to form some compound. Examples of these studies include the ones for the oxides of magnesium,<sup>5</sup> aluminum,<sup>6</sup> and lithium.<sup>7</sup>

Carbon is an element which displays "chemical effects" but which has received little attention. Strong differences in the fine structure of the *KVV* spectrum of carbon occur depending on whether carbon is bonded with silicon, a transition metal such as titanium, or with itself (as in graphite and diamond).<sup>8</sup> Few attempts, though, have been made to explain the fine structure. Graphite has been studied the most, and "nickel carbide" has been examined by several groups.<sup>9,10</sup> There remain, however, a number of carbon compounds yet to be investigated. Of particular note are the carbides of the *IVb*, *Vb*, and *VIb* transition metals. These compounds are of both theoretical and experimental interest owing to their high melting points, hardness, and metallic properties.

Consequently, the carbon Auger spectra for TiC, VC, and Cr<sub>3</sub>C<sub>2</sub> have been measured, and the results are presented here. These measurements are analyzed in conjunction with valence-band information obtained from x-ray emission work, x-ray photoelectron data, and density-of-states

calculations, and in terms of theoretical models for the Auger effect. Conclusions regarding the kinds of information present in the carbide Auger spectra will be given.

### EXPERIMENTAL

All experiments were performed in a stainless-steel ultrahigh-vacuum chamber at pressures on the order of  $3 \times 10^{-7}$  Pa. The carbide samples consisted of fine powders pressed into indium foil. Cleaning with argon-ion bombardment was sufficient to reduce all contaminants to limits below the level of detectability (~0.1%) for the Auger derivative mode  $dN/dE$ . Auger and photoelectron data were taken with a double-pass cylindrical mirror analyzer equipped with retarding grids as described by Palmberg.<sup>11</sup> A coaxial electron gun operating at normal incidence to the samples and at beam energies of 4 keV and beam currents of ~30  $\mu$ A was used to initiate the Auger spectra. The x-ray photoelectron distributions were excited with Mg *K $\alpha$*  radiation (1253.6 eV).

Conventional Auger derivative spectra were obtained using a modulation voltage of 0.5 V peak to peak. Direct Auger  $N(E)$  distributions were taken by measuring (as a function of energy) the secondary current at the first dynode of the electron multiplier with a picoammeter. Preretardation was used to slow the electrons to a constant pass energy of 100 eV. At this pass energy the analyzer energy resolution was measured to be  $1.2 \pm 0.1$  eV.

X-ray photoelectron energies for carbon 1s and valence levels were measured for all the carbides. The energy scale for these measurements was determined by calibrating the digital voltmeter which measured electron binding energy to read 284.6 eV for the 1s level of graphite.<sup>12</sup> Sample charging was minimized by providing good electrical contacts between the samples and ground and no charging was observed during Auger measurements. All spectra were signal averaged with a Nicolet 1072

Instrument Computer and were taken at a pass energy of 25 eV. Instrumental resolution was measured to be  $1.1 \pm 0.1$  eV.

To improve the resolution of the Auger data, two mathematical procedures were applied to the  $N(E)$  spectra. The first of these, suggested by Sickafus,<sup>13</sup> subtracted the secondary electron background from the measured distribution curves. The second procedure took these results and employed a Van Cittert deconvolution technique<sup>14</sup> to rid the Auger spectra of energy-dependent broadening resulting from instrumental resolution and solid-state effects in Auger emission. The broadening or resolution function that was used in the deconvolution was assumed, as in the case of Mularie and Peria,<sup>15</sup> to be approximated by the elastic peak spectrum (with attendant loss peaks) taken for a primary electron beam energy comparable to that of the Auger signal of interest. Both procedures were performed numerically on an IBM 370/168 computer. The data used for the calculations were partitioned by intervals of 1 eV.

#### RESULTS AND DISCUSSION

In Fig. 1, the derivative Auger spectra for TiC, VC, and  $\text{Cr}_3\text{C}_2$  are shown. The features of the three derivatives have been aligned to make a com-

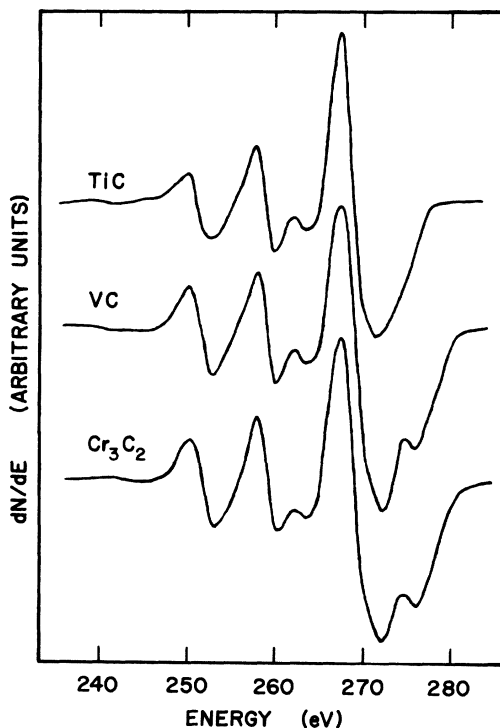


FIG. 1. Carbon Auger derivative spectra for TiC, VC, and  $\text{Cr}_3\text{C}_2$ . The peak minima have been aligned for purposes of comparison.

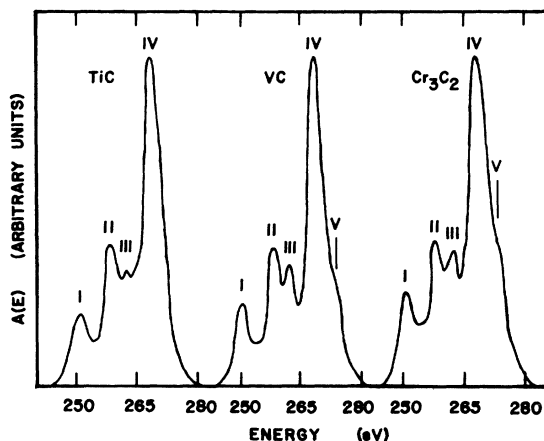


FIG. 2. Carbon Auger spectra  $A(E)$  for TiC, VC, and  $\text{Cr}_3\text{C}_2$ . The functions are the tenth iteration of a deconvolution technique to remove broadening due to instrumental resolution and solid-state loss processes.

parison of the spectra easier. The curves are essentially identical except for the minimum that appears at  $\sim 276$  eV for VC and  $\text{Cr}_3\text{C}_2$  but not for TiC. This minimum corresponds to a "shoulder" that appears in the undifferentiated spectra of VC and  $\text{Cr}_3\text{C}_2$ .

In Fig. 2, the results of the Sickafus and Van Cittert correction methods applied to the measured  $N(E)$  spectrum of each carbide is presented as  $A(E)$ . Each curve represents the tenth iteration of the Van Cittert procedure. A reconvolution of each  $A(E)$  function with its corresponding resolution function gives a curve that agrees with the measured Auger distribution (corrected by the Sickafus technique) to within  $\sim 5\%$  for the interval from 245 to 285 eV. Four peaks, labeled I–IV, are resolved for each carbide. A shoulder, labeled V, also appears for VC and  $\text{Cr}_3\text{C}_2$  and corresponds to the minimum at 276 eV mentioned previously. The energies corresponding to the maxima of peaks I–IV are given in Tables I–III; these values are compared with "calculated" energies using two theoretical models of Auger emission that will be discussed below.

The simplest approach to explain the Auger peaks of Fig. 2 is found in the Lander convolution model by assuming that  $A(E)$  is the convolution square of the density of states (DOS) for each compound.

TABLE I. Comparison of calculated and measured carbon Auger energies of TiC.

	Peak I (eV)	Peak II (eV)	Peak III (eV)	Peak IV (eV)
Measured	252.0	259.0	263.0	270.0
Calculation 1	255.9	...	263.1	270.3
Calculation 2	252.0	259.0	263.7	270.0

TABLE II. Comparison of calculated and measured carbon Auger energies of VC.

	Peak I (eV)	Peak II (eV)	Peak III (eV)	Peak IV (eV)	Peak V (eV)
Measured	252.0	259.0	263.0	269.0	274.0
Calculation 1	255.0	...	262.5	270.0	273.5
Calculation 2	252.0	258.7	263.1	269.0	...

This approach can be checked using, as assumed density-of-states functions, x-ray photoelectron valence-band spectra taken for each compound. A justification for this use is demonstrated for TiC in Fig. 3 where the carbon *K* emission data of Holliday<sup>16</sup> is compared with the valence-band DOS calculation and x-ray photoelectron spectrum of Ihara *et al.*<sup>17</sup> Figure 3 shows that the valence band is composed of two peaks, labeled I and II. According to the calculation of Ihara *et al.*, peak I is formed almost exclusively by the carbon 2*s* electrons, and peak II is formed by bonds between the carbon 2*p* electrons with the titanium 3*d* and 4*s* electrons. This claim is substantiated by the carbon *K* emission spectrum; since radiative transitions between the carbon 2*s* and 1*s* states are forbidden, only transitions from the carbon 2*p* and the metal 3*d* and 4*s* levels to the 1*s* state can occur. Consequently, only peak II appears in the emission spectrum.

A convolution of the photoelectron spectrum of Fig. 3 is shown in Fig. 4. When this function is compared with  $A(E)$  for TiC, two obvious differences can be seen. First, Fig. 4 shows a curve with only three distinguishable features, i.e., two resolved peaks and an unresolved peak appearing as a shoulder;  $A(E)$  has four resolved peaks. Second, whereas the two peaks of Fig. 4 agree closely in energy with peaks III and IV of  $A(E)$ , the relative intensities between the peaks is markedly different.

A more quantitative comparison between the convoluted photoelectron spectrum and the  $A(E)$  functions can be made by calculating the peak energies for the convolution function and then by comparing them with the measured energies. The equation used for calculation of the energies is given as

$$E = E_B(K) - E_B(P) - E_B(P') - \phi_A, \quad (1)$$

where  $E$  is the Auger peak energy,  $E_B(K)$  is the

binding energy of the carbon *K* shell,  $E_B(P)$  and  $E_B(P')$  are the energies of the maxima of the peaks like I and II appearing in the photoelectron spectrum from which the Auger electrons can come, and  $\phi_A$  is the analyzer work function. The binding energies are used as positive quantities.

The energies of the photoelectron peaks for the carbon 1*s* level and the valence band levels were measured for TiC, VC, and Cr<sub>3</sub>C<sub>2</sub>. These results are listed in Table IV. The energies for the valence peaks of TiC were found to be in good agreement with the work of Ihara *et al.*<sup>17</sup> It was also found that VC and Cr<sub>3</sub>C<sub>2</sub> have valence bands similar to that of Fig. 3, i.e., there are two peaks, I and II, with relative intensities and energies close to the values for TiC. A third peak or shoulder was discovered, however, for VC and Cr<sub>3</sub>C<sub>2</sub> near the top of the valence band. This feature is marked III in Fig. 5, in which for VC the non-self-consistent augmented-plane-wave DOS calculation of Zbasnik and Toth<sup>18</sup> is compared with the carbon *K* emission of Holliday.<sup>16</sup> Work done by Holliday<sup>16</sup> for the metal *L*<sub>2,3</sub> emission bands of VC and Cr<sub>3</sub>C<sub>2</sub> shows that the metal 3*d* and 4*s* electrons are responsible for peak III.

For each carbide, the values listed in Table IV were used according to Eq. (1) to calculate the expected Auger peak energies predicted by the Landier convolution model. These energies appear in Tables I–III and are identified under "Calculation 1." Transitions in which the Auger electrons both come from peak III of the DOS for VC and Cr<sub>3</sub>C<sub>2</sub> were not considered since the intensities would be too low to be measured; similarly, transitions involving peaks I and III for the same DOS were also not considered.

The results for calculation 1 in Tables I–III show that there is good agreement (to within ~1 eV) between the experimental and the calculated values for peaks III, IV, and V. This result is somewhat

TABLE III. Comparison of calculated and measured carbon Auger energies of Cr<sub>3</sub>C<sub>2</sub>.

	Peak I (eV)	Peak II (eV)	Peak III (eV)	Peak IV (eV)	Peak V (eV)
Measured	251.0	258.0	262.0	269.0	274.0
Calculation 1	254.9	...	262.5	270.1	273.8
Calculation 2	251.0	258.0	262.7	269.0	...

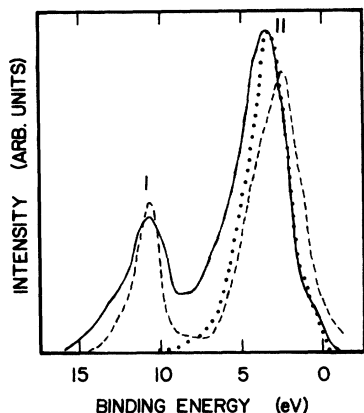


FIG. 3. Comparison of the valence-band density of states (dashed line) and the x-ray photoelectron spectrum (solid line) of Ref. 17 and the carbon *K* emission spectrum (dots) of Ref. 16 for TiC. Binding energies are referenced to the Fermi level.

deceptive for peak III, however, since the relative intensity of peak III to peak IV differs by a factor of  $\sim 2$  between the experimental and convolution data. Tables I–III also show a difference of 3–4 eV between the values for peak I. The most important feature of the tables is the lack of a peak II for calculation 1. This absence of peak II plus the discrepancy in the relative intensity of peak III occurs because the Lander model fails to account for effects such as relaxation and angular momentum coupling of the final-state holes.

A theoretical approach to Auger emission that does consider final-state effects is the intermediate coupling scheme of Asaad and Burhop.<sup>19</sup> Auger peaks (designated with spectroscopic notation) are identified with the multiplet splittings that arise from an intermediate-coupling scheme between

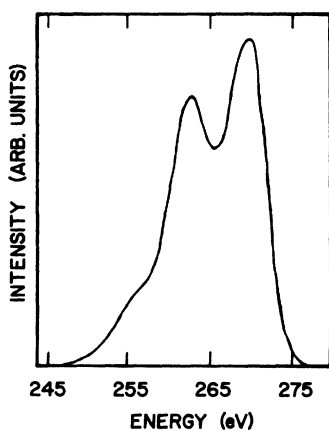


FIG. 4. Self-convolution of the x-ray photoelectron spectrum (Ref. 17) for TiC. The energy scale is determined by assigning the energy of the main maximum a value of 270 eV (see Table I).

TABLE IV. Binding energies in eV of carbon 1s and valence band levels.

Material	Peak I	Peak II	Peak III	C 1s
TiC	10.7	3.5	...	281.8
VC	11.5	4.0	0.5	282.5
Cr <sub>3</sub> C <sub>2</sub>	11.3	3.7	0.0	282.0

that of *L-S* and that of *j-j* coupling. Semiempirical calculations for the energy levels of carbon have been carried out by Siegbahn *et al.*<sup>20</sup> and these results can be applied to the carbide spectra. The lowest energy state ( $KL_1L_1, {}^1S_0$ ) calculated by Siegbahn *et al.* has an energy of 243 eV and can be identified with peak I in  $A(E)$  for all three carbides. The strongest high-energy state ( $KL_2L_3, {}^1D_2$ ) has an energy of 266 eV and can be identified with peak IV of the carbides. The multiplet terms that lie between the  ${}^1S_0$  and  ${}^1D_2$  states for the carbides can then be identified by linearly scaling down the interval between the  ${}^1S_0$  state and  ${}^1D_2$  state so that the  ${}^1S_0$  state has the energy of peak I and the  ${}^1D_2$  state has the energy of peak IV. The ( $KL_1L_2, {}^1P_1$ ) state and the ( $KL_1L_2, {}^3P_{2,1,0}$ ) states can then be associated with peaks II and III, respectively. The energies for this calculation are listed as "Calculation 2" in Tables I–III.

The results for the coupling calculation are in good agreement with the measured Auger energies for peaks II and III, signifying that final-state hole interactions can explain the existence of these peaks. This interaction argument is supported somewhat by the fact that smaller relative intensities are observed for the carbon ( $KL_1L_2, {}^3P$ ) signal (peak III) in hydrocarbon molecules (in which

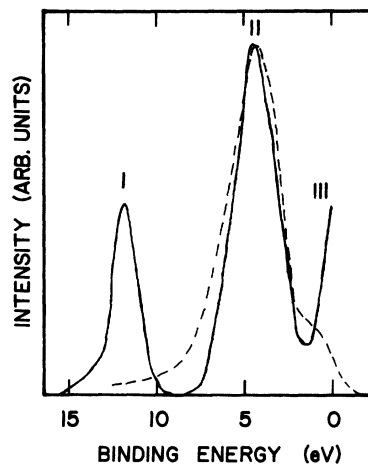


FIG. 5. Comparison of the density of states (solid line) of Ref. 18 with the carbon *K* emission spectrum (dashed line) of Ref. 16 for VC. Binding energies are referenced to the Fermi level.

coupling occurs) than are observed in the convolution spectrum of Fig. 4.

One peak is not accounted for by calculation 2. This is peak V of  $A(E)$  for VC and  $\text{Cr}_3\text{C}_2$ . In this case, the Lander model predicts that peak V is the result of electrons from both peak II and III of the DOS taking part in the Auger transition. There is no corresponding transition predicted by the coupling model.

#### CONCLUSIONS

The carbon Auger spectra of TiC, VC, and  $\text{Cr}_3\text{C}_2$  have features that can be identified in terms of both the Lander convolution model and the final-

state coupling scheme of Asaad and Burhop. Peaks I–III for the carbide Auger spectra can be attributed to the coupling interaction. Peak IV can be explained by either theoretical model. Peak V is explained only by the convolution model. Thus, even though the carbides have well defined band structures, the Auger spectra still reflect predominantly the final-state electronic configuration rather than the initial one.

#### ACKNOWLEDGMENT

The authors would like to thank Dr. E. N. Sickafus for his helpful discussions and advice.

---

\*Work supported by the Division of Materials Research of the NSF under Contract Nos. DMR 76-20038 and DMR 74-00402.

†Present address: Ford Motor Co., Dearborn, Mich. 48121.

<sup>1</sup>J. J. Lander, *Phys. Rev.* **91**, 1382 (1953)

<sup>2</sup>G. F. Amelio, *Surf. Sci.* **22**, 301 (1970).

<sup>3</sup>G. F. Amelio and E. J. Scheibner, *Surf. Sci.* **11**, 242 (1968).

<sup>4</sup>M. A. Smith and L. L. Levenson (unpublished).

<sup>5</sup>M. Salmeron, A. M. Baro, and J. M. Rojo, *Surf. Sci.* **53**, 689 (1975).

<sup>6</sup>P. H. Citrin, J. E. Rowe, and S. B. Christman, *Phys. Rev. B* **14**, 2642 (1976).

<sup>7</sup>H. H. Madden and J. E. Houston, *J. Vac. Sci. Technol.* (to be published).

<sup>8</sup>See, for example, the spectra given by C. C. Chang, in *Characterization of Solid Surfaces*, edited by P. F. Kane and B. Larrabee (Plenum, New York, 1974), p. 527.

<sup>9</sup>J. P. Coad and J. C. Riviere, *Surf. Sci.* **25**, 609 (1971).

<sup>10</sup>M. Salmeron, A. M. Baro, and J. M. Rojo, *Phys. Rev. B* **13**, 4348 (1976).

<sup>11</sup>P. W. Palmberg, *J. Vac. Sci. Technol.* **12**, 379 (1975).

<sup>12</sup>F. R. McFeely, S. P. Kowalczyk, L. Ley, R. G. Carell, R. A. Pollak, and D. A. Shirley, *Phys. Rev. B* **9**, 5268 (1974).

<sup>13</sup>E. N. Sickafus, *Rev. Sci. Instrum.* **42**, 933 (1971).

<sup>14</sup>H. H. Madden and J. E. Houston, *J. Appl. Phys.* **47**, 3071 (1976).

<sup>15</sup>W. M. Mularie and W. T. Peria, *Surf. Sci.* **26**, 215 (1971).

<sup>16</sup>J. E. Holliday, *J. Appl. Phys.* **38**, 4720 (1967).

<sup>17</sup>H. Ihara, Y. Kumashiro, and A. Itoh, *Phys. Rev. B* **12**, 5465 (1975).

<sup>18</sup>J. Zbasnik and L. E. Toth, *Phys. Rev. B* **8**, 452 (1973).

<sup>19</sup>W. N. Asaad and E. H. S. Burhop, *Proc. Phys. Soc. Lond.* **71**, 369 (1958); W. N. Asaad, *Proc. R. Soc. Lond. A* **249**, 555 (1959); W. N. Asaad, *Nucl. Phys.* **44**, 399 (1963); **44**, 415 (1963); **63**, 337 (1965); **66**, 494 (1965).

<sup>20</sup>K. Siegbahn *et al.*, in *Atomic, Molecular and Solid Structure Studied by Means of Electron Spectroscopy, ESCA (Electron Spectroscopy for Chemical Analysis)* (Almqvist and Wiksell Boktryckeri AB., Uppsala, 1967).