The entropy calculations described here thus support crystallographic data by confirming the existence of an entropy due to the disorder, and show a gradual change to an ordered structure as the temperature is lowered.

The uncertainties pertinent to the calculations are the precision uncertainties; additional uncertainties affecting the absolute values would be expected to cancel out almost completely. The precision uncertainty was taken as twice the estimated standard deviation (S.D.) of the measured heat capacities from the smoothed data. In most cases 2 S.D. was 0.003 to 0.004 cal $°K^{-1}$ $g\text{-atom}^{-1}$; 2 S.D. was highest (0.022) in the region shown in Fig. 1. In estimating uncertainties of integration, it was assumed that the errors of the smoothed heat capacity data were always 2 S.D. (that is, that absolute values of error were additive). However, it was assumed that the difference between the heat capacities of orthorhombic and monoclinic sulfur was random (that is, that errors added to form the square root of the sum of their squares). The errors of extrapolation to 0°K and of ΔH_e and T_e were considered too small to be significant in the presence of the errors already considered. The procedure used gives a conservative estimate of the uncertainty.

Measurements were made by adiabatic calorimetry. The main modification of the basic design (*2*) was the addition of an outer shield of copper (gold-plated on the outside) to the calorimeter. This was done to reduce the difference in surface temperature gradients between the empty and filled calorimeter. The system accuracy was checked by measuring the heat capacity of *n*-heptane. The largest deviations from selected values (*3*) were 0.2 percent. The results for solid sulfur below T_e agree with other determinations (*4*) within expected limits of accuracy. The sulfur measurements were made under a low pressure of helium (well below atmospheric pressure at the melting point of sulfur) and thus are essentially equal to constant-pressure measurements at a low pressure.

A small calorimeter filling tube made of Monel and soldered with tin (lightly alloyed to prevent "tin disease") was exposed to any sulfur that might have vaporized and migrated to it. The amount of tin exposed was minute. The amount of Monel exposed was small, and an experiment showed that Monel was attacked only very slowly, even by molten sulfur. Therefore, chemical reactions should not have affected the results.

The leak test performed at the beginning of the measurements could not be repeated afterward, because the calorimeter ruptured (apparently because of volume changes accompanying the transformation of solid sulfur near T_e) during later studies. The copper shield of the calorimeter acted as a "leak detector"; the heat effect of reaction between it and sulfur was immediately apparent. Between the low-temperature studies and the rupture, the calorimeter had been used at temperatures as high as 434°K. The heat exchange rates during this period were essentially the same as those observed with the empty calorimeter before it was filled with sulfur; they showed no evidence of any reaction between copper and sulfur. The calorimeter was cycled between temperatures around T_e and cryogenic temperatures during the low-temperature measurements without causing a large precision uncertainty. Therefore leakage was not a problem during the low-temperature measurements.

The sulfur was obtained from the National Bureau of Standards, and a study of the fraction melted versus temperature indicated that it contained 10^{-5} mole fraction of impurities soluble in the liquid and insoluble in the solid. No anomalous behavior was noted in the heat capacities near the boiling point of water, and water is not likely to have been present in a significant amount (*5*).

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Electronic Structure and Catalytic Behavior of Tungsten Carbide

Abstract. *Tungsten carbide has been shown to be an effective catalyst for a number of reactions that are readily catalyzed by platinum, but not at all by tungsten, and it was speculated that this behavior is due to changes in the electron distribution when carbon is added to tungsten. A test of this hypothesis, made by measuring the valence band x-ray photoelectron spectrum of tungsten carbide and comparing it with the spectra of tungsten and platinum, shows that, near the Fermi level, the electronic density of states of tungsten carbide more nearly resembles that of platinum than that of tungsten.*

Tungsten carbide has been found (*1*) to be an effective catalyst for a number of chemical reactions (particularly the isomerization of 2,2-dimethylpropane) that are catalyzed readily by the scarce metal platinum, but not at all by tungsten. A growing body of experimental data (*2*) indicates a close relationship between catalytic activity and the density of *d*-like states at the Fermi level, the energy below which all the electronic states are occupied and above which they are empty. It is therefore of interest to investigate the state density of WC, and compare it to those of W and Pt. We have used x-ray photoelectron spectroscopy (XPS) to study the valence band and core levels of WC; our results show that this compound is more like Pt than it is like W.

The sample studied was a powder (−200 mesh), more than 99.9 percent pure (by flame spectroscopic analysis), and was single phase (x-ray diffraction showed sharp lines and no extra lines). A thick coating of the powder was pressed onto an annealed Au substrate. The powder layer was sufficiently thick and evenly distributed that the intense 4*f* lines of the Au substrate could not be detected. Nonmonochromatized Mg $K\alpha$ radiation was used for the measurement, at a base pressure of 2×10^{-9} torr. Initially, the sample was cleaned for 22 minutes by bombardment with Ne ions, at 4×10^{-5} torr, 1.0 kev, and 3.6×10^{-6} amp. This was sufficient to reduce the intensities of the 1*s* lines of oxygen and contaminant carbon (the latter chemically shifted from that of carbon in WC) to 6 and 10 percent, respectively, of their initial values. Measurements were made over successive 7-minute periods, during which no contaminant buildup was detectable, separated by 6-minute cleaning periods.

Raw data for the valence band XPS spectrum of WC are compared in Fig. 1 with those of clean Pt (*3*) and W [the (111) plane] (*4*). The three spectra are placed within 0.1 ev in absolute position with respect to one another; the position of the Fermi level, E_F, is assigned with respect to a standard line (Au $4f_{5/2}$). The density of states at the Fermi level, $N(E_F)$, of WC is intermediate in character between that of W, where the Fermi level falls in a region of low density of *d*-like states, and that of Pt, where the Fermi level falls in a region of high density of *d*-like states. Core level measurements were in good agreement with earlier results (*5, 6*). In WC the C 1*s* level exhibited a binding energy about 1.8 ev lower than in contaminant C, and the W 4*f* levels a binding energy about 0.3 ev higher than in W. Since charge transfer from a site increases core level binding, these results are usually interpreted as implying charge transfer from the W to the C atoms in WC (*5, 6*), although the situation is complicated by many factors such as crystal potential (*6*), final state relaxation, Fermi level shifts, and other effects.

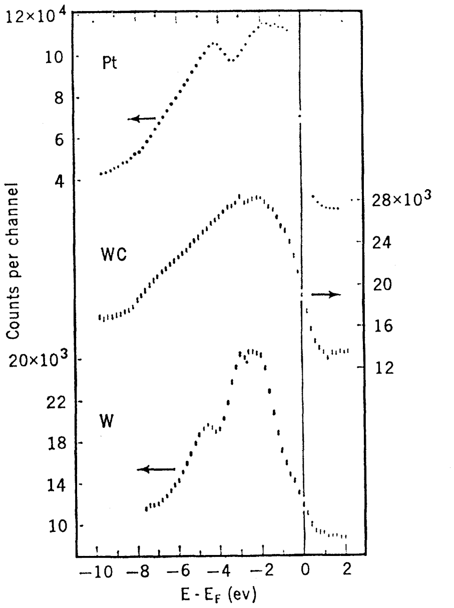

Fig. 1. Valence band XPS spectra of WC, Pt (*3*), and W [the (111) plane] (*4*). Raw data are shown in each case. For W and WC the length of the data bars represents the standard deviation (70 percent statistical confidence level). For Pt, the diameter of the data points is equal to or greater than the standard deviation. The Fermi level has been placed so that a standard line, Au $4f_{5/2}$, lies 87.6 ev below it.

The experimental trend in $N(E_F)$ in Fig. 1 is compatible with available theoretical densities of states. A calculation for Pt (Fig. 2a) (*7*) shows that E_F falls in a region of high density of states, as in Fig. 1. A nonrelativistic calculation for body-centered cubic W gives the results shown in Fig. 2c (*8, 9*). If the band is filled with six electrons, which is appropriate for W, E_F will fall in a broad region of low density of states, again consistent with Fig. 1. No band calculation has been reported for WC where the W atom falls in a simple hexagonal lattice. However, a relativistic calculation (*10*) has been made for Re (Fig. 2b), a hexagonal close-packed metal next to W in the periodic table, and if the histogram for Re is again filled with the six electrons corresponding to W, E_F falls in a region with an appreciably higher density of states. The increase obtained here is consistent with the results of Fig. 1, but this is an oversimplification of what occurs; details of the density of states will be modified by the differing sublattice structure (simple versus close-packed hexagonal) and F_F need not fall at a level corresponding to a band filling of exactly six since such factors as charge transfer will modify this number. We believe that an essential factor, leading to an increase in $N(E_F)$, is the change from a body-centered structure, where E_F falls in a broad region of low density of states, to a hexagonal structure, where E_F falls in a region of high density of states.

Of course, the observation of a more platinum-like $N(E_F)$ in WC does not provide a complete explanation for its observed catalytic behavior. We believe that a high $N(E_F)$ is a necessary but not sufficient condition for high catalytic activity. For instance, the density of states alone might lead one to expect transition metals such as V or Ta to be an effective substitute for Pt as well, whereas they are not; in general, the lighter transition metals of a series, even with a high $N(E_F)$, show little or no catalytic activity compared to the metals at the heavy end. However, these lighter metals do not display the exchange enhancement of the magnetic susceptibility leading to strong paramagnetism (or ferromagnetism) which is characteristic of the heavier elements such as Pt. Therefore, another important condition for high catalytic activity may be related to the magnetic properties of the metal. It remains to be seen whether WC does show strong susceptibility enhancement, and the magnetic properties of WC should be the object of further studies. To press this hypothesis further, the catalytic activity of metals that exhibit both high $N(E_F)$ and high susceptibility enhancement should be tested. A suitable example might be CrB_2, which is known to exhibit an enhanced susceptibility and have a high $N(E_F)$ (*11*).

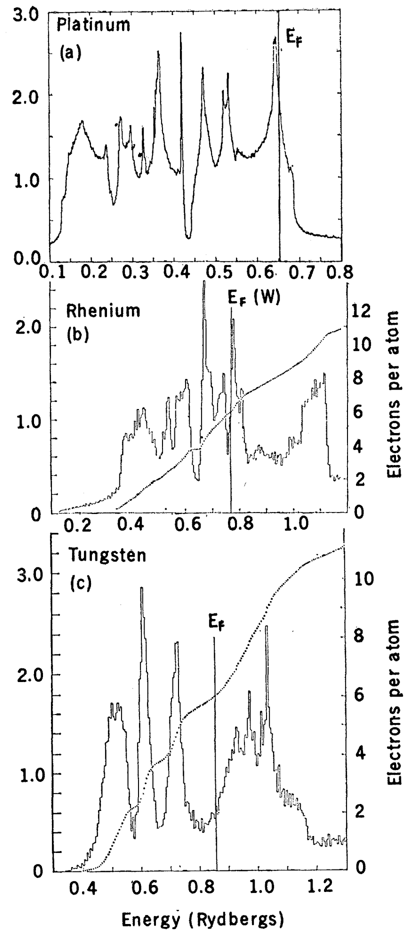

Fig. 2. Calculated total density of states. (a) Relativistic augmented plane wave (APW) calculation for face-centered cubic Pt [from Mueller *et al.* (*7*)]. (b) Relativistic APW calculation for hexagonal close-packed Re [from Mattheiss (*10*)]. The position of $N(E_F)$ for W is shown. (c) APW calculation for body-centered cubic W [from Mattheiss (*8*)].

So far we have discussed the qualification of a material as a catalyst in terms of bulk properties, but the point is often made that, because catalysis is a surface phenomenon, it is the surface electronic structure that should be considered. This argument is no doubt quite valid. However, the surface electronic structure is directly related to the bulk structure and, in practice, the bulk properties seem to give good correlation with surface reactivity. An example is the phenomenon of surface film formation in corrosion, an area in which H. H. Uhlig has had considerable success in explaining a myriad of surface passivation phenomena on the basis of bulk electronic structure (*12*).

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27 December 1973

X-ray Photoelectron Spectroscopic Studies of Interactions in Multicomponent Metal and Metal Oxide Thin Films

Abstract. Changes in chemical oxidation states in alloys and at solid-solid interfaces were monitored by using x-ray photoelectron spectroscopy. For an oxidized Nichrome surface, the chromium component was selectively converted to chromic oxide while nickel remained in the metallic state. When this surface was overlaid with a 20-angstrom-thick aluminum film, the chromic oxide was reduced to chromium and the aluminum was oxidized to aluminum oxide in a reaction zone consisting of no more than 10 angstroms of the interface. This scheme appeared general for solid-solid contacts and was predicted, to a first approximation, by bulk thermodynamic free energies.

Much of the research on the structure and chemical composition of thin film surfaces during the last several decades was restricted to relatively thick layers because of the sample requirements of the available analytical techniques (*1*). Recently, however, there has been an expansive development of a variety of new spectroscopic methods, such as electron diffraction, Auger spectroscopy, secondary ion mass spectroscopy, ion scattering spectrometry, and microprobe methods, which are capable of characterizing structure and composition for material present in only fractional monolayers. Of particular interest is x-ray photoelectron spectroscopy (XPS); in addition to providing elemental analyses, this technique measures the electron binding energy, and chemical shifts of this energy are often directly relatable to molecular structure and bonding.

Considerable emphasis is currently being placed on characterizing the surface structure of multicomponent substrates, which are attractive as new materials in catalysis, corrosion inhibition, and electrochemistry. For example, Auger spectroscopic studies indicate differences between surface and bulk concentrations in alloys (*2*). Further changes have been noted after an alloy surface is exposed to oxygen, due to the preference of oxygen for one of the alloy components (*3*). Ion microprobe studies of Fe_2O_3 doped with Al have examined the passivating effect this treatment has on Fe_2O_3 substrates, and excess surface concentrations of Al have been noted (*4*). Several low-energy electron diffraction studies have elucidated the types of surface interactions that are involved in these multicomponent systems. For example, it has been suggested (*5*) that Cs and O absorbed on the (100) or (112) planes of W form a Cs-O-W double layer regardless of which species was deposited first.

Perhaps the best chemical information on these systems can be obtained by XPS techniques, although there are few examples from the literature to support this claim. The oxidation of a NiCu

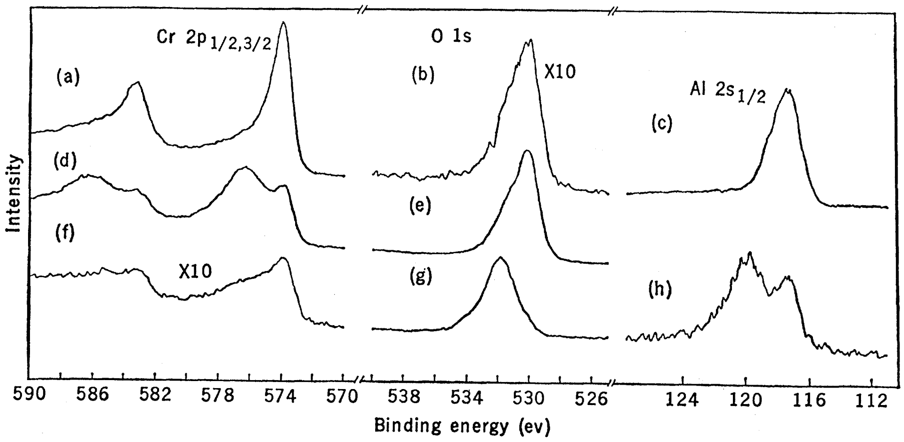

Fig. 1. X-ray photoelectron spectra. (a) Chromium chip evaporated at 1×10^{-7} torr onto Cu foil. (b) Residual oxygen from the sample in (a). (c) Aluminum wire evaporated at 1×10^{-7} torr onto Cu foil. (d) and (e) Oxidized Cr surface from (a) after exposure to 0.01 atm of oxygen for 30 seconds. An identical spectrum is obtained for the Cr component in an oxidized Nichrome film. (f), (g), and (h) Chromium surface (d) overlaid with about 20 Å of Al. Note the relative decrease in oxide shoulder on the Cr $2p_{1/2,3/2}$ peaks and the shift of the O 1*s* peak to 532.0 ev, now characteristic of Al_2O_3.