

## X-Ray Photoelectron Spectroscopic Studies of CrO<sub>2</sub> and Some Related Chromium Compounds

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Core-electron and valence-band regions of crystalline CrO<sub>2</sub>, CrOOH, Cr<sub>2</sub>O<sub>3</sub>, and K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> have been studied. The XPS spectrum of the valence band region of CrO<sub>2</sub> is interpretable in terms of Goodenough's band-structure model, and the finite density of states at the Fermi level for this metallic compound is readily apparent, but the band profile shows no detectable change on traversing the Curie temperature. Whereas the ratio of the multiplet splittings recorded for Cr 3s levels in CrO<sub>2</sub> and Cr<sub>2</sub>O<sub>3</sub> are in reasonable agreement with theory, discrepancies were noted between observed and expected multiplet intensity ratios. Some evidence for shake-up satellites was also noted. The smaller binding energies of core-electron levels in the Cr<sup>4+</sup> solid (CrO<sub>2</sub>) compared with the corresponding binding energies in Cr<sup>3+</sup> compounds (Cr<sub>2</sub>O<sub>3</sub> and CrOOH) are also discussed.

Among the oxides of chromium, CrO<sub>2</sub> is of particular interest in view of its striking electronic properties. It displays quasi-metallic behavior (resistivity at room temperature 10<sup>-4</sup> ohm cm) and ferromagnetism with a Curie temperature of ca. 125°C (1, 2); and these properties are qualitatively explicable in terms of the band-structure model proposed by Goodenough (3, 4). It, therefore, seemed desirable to record the photoelectron spectra of this solid both above and below the Curie temperature; and also to compare the satellites observed in the core-electron peaks of CrO<sub>2</sub> with the corresponding satellites in related compounds of chromium. The latter comparison should throw some light (especially since in CrO<sub>2</sub> there is nominally Cr<sup>4+</sup>) on the continuing debate as to the various possible origins of such satellites, see Refs. (5-10) for fuller details. Accordingly, we have examined powdered samples of CrO<sub>2</sub> (kindly provided

by Prof. K. S. W. Sing, Brunel University, England), CrOOH, Cr<sub>2</sub>O<sub>3</sub> and K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>.

### Experimental

Most of the X-ray photoelectron spectra were recorded with a McPherson ESCA 36 electron spectrometer, employing AlK<sub>α</sub> radiation (1486.6 eV); some of the earlier measurements were made on an AEI ES 200 instrument. The samples could be directly mounted on aluminium plates by application of pressure, and the binding energies of the various photoelectron peaks were calibrated with respect to the Au 4f<sub>7/2</sub> peak taken as 84.0 eV, minute amounts of gold having been deposited by sublimation within the sample chamber of the spectrometer. Cr<sub>2</sub>O<sub>3</sub> and K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> (special grade chemicals, Nakarai Chemicals, Ltd.) were used without further

purification; some difficulty arose with  $\text{CrO}_2$  itself in that it could not be fully freed of adsorbed oxygen. Moreover argon-ion bombardment converted the surface to  $\text{Cr}_2\text{O}_3$ .

### Results and Discussion

The XPS spectrum of the  $\text{CrO}_2$  was recorded after the sample had first been heated to and maintained at  $200^\circ\text{C}$  inside the spectrometer. The spectrum was also taken after sample temperature had been dropped to  $45^\circ\text{C}$  (see Fig. 1 which also shows the corresponding core peaks, recorded at room temperature, for a sample that had had prolonged exposure to air). Note that the  $\text{Cr } 2p$  and  $\text{Cr } 3p$  peaks are slightly broadened and the higher binding energy satellite peak of  $\text{Cr } 3s$  peak is enhanced after exposure of the sample to the air. Heated samples showed the same behavior when they were left in the air for several days; and these effects seem to be associated with adsorbed oxygen. The spectra at  $45^\circ\text{C}$  and  $200^\circ\text{C}$ , are however believed to be essentially free from the effects of adsorption.

There were no detectable differences between the spectra obtained above and those obtained below the Curie point. In particular, there was on change, within experimental error, in the multiplet splitting of the  $\text{Cr } 3s$  spectrum indicating that the ferromagnetic ordering of spins of  $3d$  electrons is unimportant so far as the magnitude of this particular (cf. Ref. (11)) multiplet splitting is concerned.

The spectrum in the region of  $\text{O } 2s$  and valence-electron bands (Fig. 2) also exhibited no appreciable change above and below the Curie point, and the observed spectrum is interpretable in terms of Goodenough's model of the band scheme of  $\text{CrO}_2$  (see Fig. 3) (2-4). The broad, strong band observed at 21 eV is attributable to the  $\text{Me-O } \sigma$  band of the scheme symbolized in Fig. 3. The observed spectrum shows a broad band at 5 eV and a rather sharp one around 2.0 eV. These features are again in accord with Goodenough's model; the former is assigned to the narrow  $\text{Me-O } \pi$  band and the latter embraces the localized  $t2g''$  level and the half-filled  $\pi^*$  band. Evidently the XPS spectrum does not separate the  $t2g''$  and the  $\pi^*$ . It is interesting to note that, in the observed spectrum, the Fermi level is located on the low-energy tail of the last filled band; and there is clearly a finite density of states at the Fermi level. This is consistent with the metallic behavior of  $\text{CrO}_2$  and supports the idea that the last band does indeed consist of the localized  $t2g''$  level and the half-filled  $\pi^*$  band.

In Fig. 4 we compare the XPS spectra of  $\text{Cr}_2\text{O}_3$ ,  $\text{CrOOH}$ ,  $\text{CrO}_2$ , and  $\text{K}_2\text{Cr}_2\text{O}_7$ . The relative intensity of the bands in the region below 5 eV is smaller in  $\text{CrO}_2$  than in  $\text{Cr}_2\text{O}_3$  or  $\text{CrOOH}$ , as would be expected from the known decrease in the number of  $3d$  electrons. With  $\text{K}_2\text{Cr}_2\text{O}_7$  which possesses no  $3d$  electron, there is, as expected, no corresponding band at ca 5 eV.

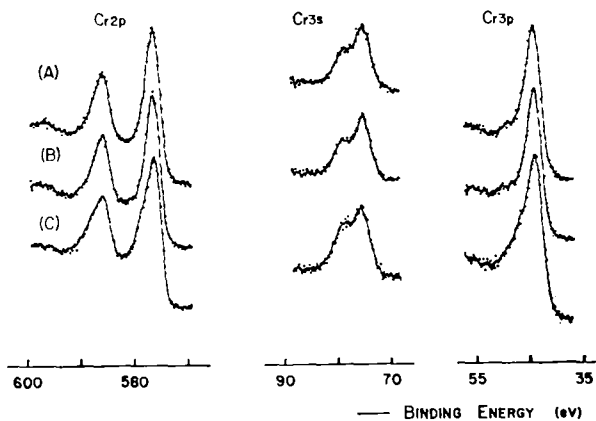


FIG. 1. XPS spectra of  $\text{CrO}_2$ ; (A) at  $200^\circ\text{C}$ , (B) at  $45^\circ\text{C}$ , (C)  $\text{CrO}_2$  left in the air for a long period.

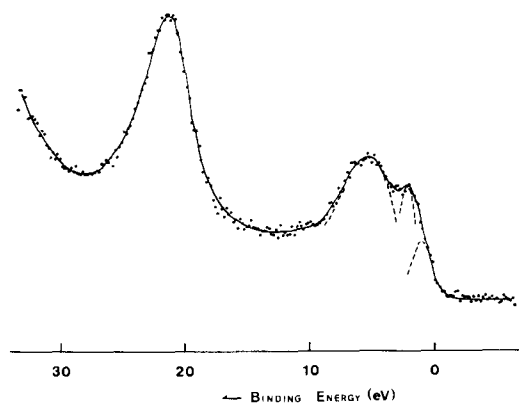


FIG. 2. XPS spectrum in the region of the O 2s and valence bands of CrO<sub>2</sub>.

The changes in valence band profiles resulting from changes in *d* electron population have their analogs in the deeper-lying electronic energy levels. Thus, the 3s multiplet splitting is naturally totally absent in diamagnetic K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, where there is but a single sharp 3s peak, in contrast to the doublets displayed by the other three compounds. The magnitudes of the multiplet splittings are 3.8, 3.9, and 3.5 eV for Cr<sub>2</sub>O<sub>3</sub>, CrOOH, and CrO<sub>2</sub> respec-

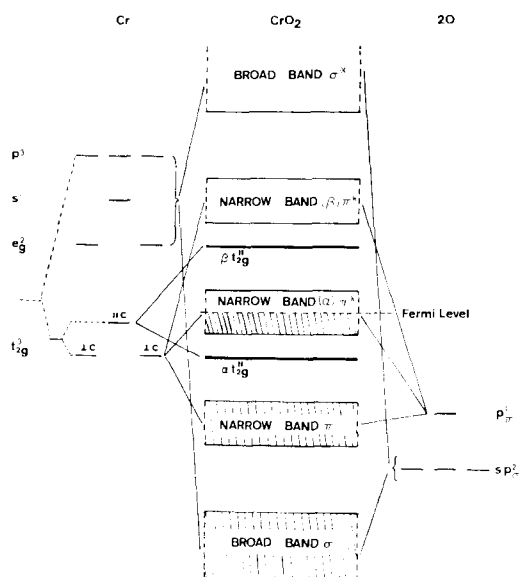


FIG. 3. Goodenough's model of the band scheme of CrO<sub>2</sub>.

tively. It is known (12) that, when the 3s core-electron levels of a paramagnetic transition metal ion is split by the 3d valence electrons, the magnitude of the splitting,  $\Delta E$ , is related

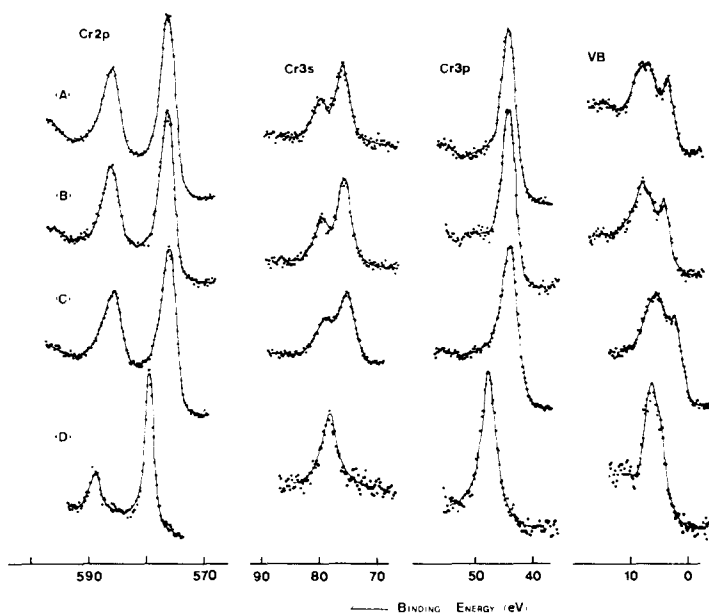


FIG. 4. XPS spectra of: (A) Cr<sub>2</sub>O<sub>3</sub>, (B) CrOOH, (C) CrO<sub>2</sub>, and (D) K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>.

to the total spin of the  $3d$  electrons,  $S$ , by the relationship:

$$\Delta E \propto H_x(2S + 1)$$

where  $H_x$  is the exchange integral between a  $3s$  and a valence-shell orbital. Since  $S = 1$  for  $\text{Cr}^{4+}$  compounds such as  $\text{CrO}_2$ , and  $S = 3/2$  for  $\text{Cr}^{3+}$  compounds such as  $\text{Cr}_2\text{O}_3$  then, provided  $H_x$  is assumed to be constant for each set, the ratio  $\Delta E(\text{Cr}^{4+})/\Delta E(\text{Cr}^{3+})$  is expected to be 0.75. The ratio found experimentally for  $\Delta E(\text{CrO}_2)/\Delta E(\text{Cr}_2\text{O}_3)$  is about 0.9 which is tolerably close to the theoretical value if we take into account the accuracy of the method. There does, however, seem to be an appreciable discrepancy between the observed intensity ratios of the multiplet peaks from those theoretically expected (13) in the free-ion model; the expected intensity ratio of the higher-binding-energy peak to the lower-binding-energy one should be 0.5 for  $\text{Cr}^{4+}$  and 0.6 for  $\text{Cr}^{3+}$ , the ratio in the  $\text{CrO}_2$  spectrum is bigger than in the  $\text{Cr}_2\text{O}_3$  spectrum. "Abnormal" ratios arise from the borrowing of intensity by other satellites (see full discussion by Kowalczyk et al (13) with reference to  $\text{Mn}^{2+}$  salts).

The  $\text{Cr } 2p$  spectrum of  $\text{CrO}_2$  as well as those of  $\text{Cr}_2\text{O}_3$  and  $\text{CrOOH}$  are considerably broader than the  $\text{Cr } 2p$  spectrum of  $\text{K}_2\text{Cr}_2\text{O}_7$ . It is possible that, for the three paramagnetic Cr compounds, the  $\text{Cr } 2p$  peaks are broadened because of the effect of the multiplet splitting due to the interaction with  $3d$  electrons. It should be noted also that the magnitude of the spin-orbit splitting between  $2p \ 1/2$  and  $2p \ 3/2$

peaks is different for different valency states of chromium; it is 9.9 eV both in  $\text{Cr}_2\text{O}_3$  and  $\text{CrOOH}$ , 9.7 eV in  $\text{CrO}_2$ , and 9.3 eV in  $\text{K}_2\text{Cr}_2\text{O}_7$ . The above values are consistent with the results reported by Allen et al. (14), who observed a splitting of 9.7–9.9 eV in  $\text{Cr}^{3+}$  compounds and 8.7–9.4 eV in  $\text{Cr}^{6+}$  compounds. Seemingly, the splitting decreases with the decrease of the number of  $3d$  electrons. The intensity of  $\text{Cr } 2p \ 1/2$  peak is about half of that of  $\text{Cr } 2p \ 3/2$  in the cases of  $\text{CrO}_2$ ,  $\text{Cr}_2\text{O}_3$ , and  $\text{CrOOH}$ , as it is usually expected, while it is exceptionally small in the case of  $\text{K}_2\text{Cr}_2\text{O}_7$ .<sup>1</sup>

The observed binding energies of core-electron levels are summarized in Table I. According to Allen *et al.*,<sup>2</sup> the binding energy of  $\text{Cr } 2p \ 1/2$  peak is 586.2–586.9 eV and that of  $\text{Cr } 2p \ 3/2$  peak is 576.4–577.0 eV in  $\text{Cr}^{3+}$  compounds, while the former is 588.1–589.1 eV and the latter is 578.3–579.8 eV in  $\text{Cr}^{6+}$  compounds.

Thus, in general, the binding energies are smaller in  $\text{Cr}^{3+}$  compounds than in  $\text{Cr}^{6+}$  compounds as expected on a simple formal charge argument for the chromium metal ion. In effect, the binding energies obtained of  $\text{Cr}_2\text{O}_3$  and  $\text{CrOOH}$  are smaller than the corresponding values of  $\text{K}_2\text{Cr}_2\text{O}_7$ . But in this regard,  $\text{CrO}_2$  appear to be abnormal; the

<sup>1</sup> The intensity ratio observed here agrees with that reported by Helmer(17).

<sup>2</sup> Their results have been corrected by taking the reference  $\text{Au } 4f \ 7/2$  as 84.0 eV, and their corrected values for  $\text{Cr}_2\text{O}_3$  and  $\text{K}_2\text{Cr}_2\text{O}_7$  agree well with those obtained in the present study.

TABLE I

BINDING ENERGIES (eV) OF  $\text{K}_2\text{Cr}_2\text{O}_7$ ,  $\text{CrO}_2$ ,  $\text{CrOOH}$ , AND  $\text{Cr}_2\text{O}_3$ 

	$\text{K}_2\text{Cr}_2\text{O}_7$	$\text{CrO}_2$	$\text{CrOOH}$	$\text{Cr}_2\text{O}_3$
Cr2p 1/2	589.1 (588.8) <sup>a</sup>	586.0	586.9	586.7 (586.5) <sup>a</sup>
Cr2p 3/2	579.8 (579.4) <sup>a</sup>	576.3	577.0	576.8 (576.8) <sup>a</sup>
Cr3s	79.0	75.1	75.8	75.5
(Splitting) <sup>a</sup>	0	3.5	3.9	3.8
Cr3p	47.6	43.5	44.1	44.0
O1s	530.5 (530.0) <sup>a</sup>	529.3	531.4	530.8 (530.5) <sup>a</sup>

<sup>a</sup> ( )—data from the work of Allen et al. (14).

TABLE II

ENERGIES (IN eV) OF THE EXTRA PEAKS OBSERVED ON THE HIGHER-BINDING-ENERGY SIDE OF THE MAIN PEAK

Main peak	K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	CrO <sub>2</sub>	CrOOH	Cr <sub>2</sub> O <sub>3</sub>
Cr 2p 1/2	~15	~11	~11	~11
Cr 2p 3/2	~15	—	—	—
Cr 3p	~15	~11.5	~11.3	~11.5
O 1s	~10.5	~10	~9.5	10 ~ 11.0
	~21	~16.5	~16.5	~16.5
	~29	~26	~25.5	~25.5

binding energy of each core-electron peak of chromium in CrO<sub>2</sub> is smaller than the corresponding value of Cr<sub>2</sub>O<sub>3</sub>, although, if there were a linear correlation with oxidation number and binding energy it would be expected to fall in between the values of Cr<sub>2</sub>O<sub>3</sub> and K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>. On the other hand, the separation between the O 1s and Cr 2p 1/2 (or Cr 2p 3/2) peaks is larger in CrO<sub>2</sub> and CrOOH, as one should expect from the difference in the formal charges. A similar anomaly as regards the binding energy has been reported to occur in other highly conductive materials such as PbO<sub>2</sub> (16) and Ti<sub>2</sub>O<sub>3</sub> (17), and one explanation (16) forwarded for this anomaly is bound up with the alleged large contribution of conduction electrons for the relaxation of a core-hole state in "metallic" solids. Another explanation for the smaller binding energy of metal core-electrons in CrO<sub>2</sub> might be possible in terms of the Madelung-potential argument discussed more fully elsewhere (18, 19). The lattice potentials and the atomic charges along the lines outlined by Parry (19) is under calculation.

Several extra peaks were observed on the higher-binding-energy sides of core-electron peaks. The energy separations of these extra peaks from the main core-electron peaks are listed in Table II.<sup>3</sup> In the cases of CrO<sub>2</sub>, Cr<sub>2</sub>O<sub>3</sub>, and CrOOH, the extra peaks accompanying the Cr 3p and Cr 2p peaks are relatively strong,

<sup>3</sup> We have attributed the extra peak in the Cr 2p spectra of CrO<sub>2</sub>, Cr<sub>2</sub>O<sub>3</sub>, and CrOOH to the one accompanying Cr 2p 1/2 peak, because the corresponding peak accompanying Cr 2p 3/2 is likely to be hidden under Cr 2p 3/2 peak.

and their energy separations from the main peaks are almost the same among these three compounds. On the other hand, extra peaks are weakly observed in the Cr 2p and Cr 3p spectra of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> with an energy separation from main peak appreciably different from that of the above three compounds. It is not easy to decide whether the extra peaks are due to an energy loss, or to a shake-up process (20). The latter is more likely since the extra peaks observed in the O 1s spectra are slightly different in energy from those in the Cr 2p and Cr 3p regions. In the crystals of CrO<sub>2</sub>, Cr<sub>2</sub>O<sub>3</sub>, and CrOOH, a chromium atom is octahedrally surrounded with six oxygen atoms, whereas it is tetrahedrally surrounded with four oxygen atoms in K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>. Thus the difference of the feature of the extra peak mentioned above seems to be reflecting the difference in the coordination of oxygen atoms around a chromium atom.

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