

Effects of Chemical Combination on X-Ray $K\alpha$ Emission Spectra of Chromium

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Asymmetry indices, chemical shifts and full widths at half maximum intensity (FWHM) of the chromium $K\alpha_1$ and $K\alpha_2$ x-ray emission lines were studied in chromium metal, some of its divalent, trivalent, tetravalent and hexavalent compounds, and minerals, catalysts and glassy materials by an x-ray fluorescence excitation method. The asymmetry indices were found to depend on the number of unpaired 3d electrons. The chemical shifts, spin-orbit splittings, asymmetry indices and the half-widths of both the X-ray emission lines show interesting trends with the oxidation state of chromium.

INTRODUCTION

X-ray emission spectra are known^{1–9} to be influenced by the chemical combination of x-ray emitting atoms with different ligands. The effects of the chemical combination, however, are not large and a theoretical interpretation of these effects has not been established completely. Therefore, chemical effects have rarely been utilized in the characterization of materials. The purpose of this work was to study the chemical effects and to discuss their applications to chromium in various materials. In particular, the asymmetry of $K\alpha_1$ and $K\alpha_2$ lines and their widths, separations and chemical shifts in divalent, trivalent, tetravalent and hexavalent compounds of chromium were examined and these effects were employed to characterize samples of minerals, catalysts and glasses.

EXPERIMENTAL

Preparation of compounds

Cr_2O_3 , CrO_3 , K_2CrO_4 , Na_2CrO_4 , $\text{K}_2\text{Cr}_2\text{O}_7$, $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ and NiCrO_4 were high-purity samples obtained commercially. LaCrO_3 was prepared by the thermal decomposition of the nitrates of lanthanum and chromium. Chromium dioxide was obtained by heating chromium(III) hydroxide in oxygen at 623 K. The chromites of magnesium and cobalt were synthesized by fusing their oxides with Cr_2O_3 . Ba_2CrO_4 was made by mixing and heating mixtures of BaCrO_4 , Cr_2O_3 and $\text{Ba}(\text{OH})_2$.^{10,11} Sr_2CrO_4 was prepared in a similar manner. Chromium(II) acetate dihydrate, $[\text{Cr}(\text{OCOCH}_3)_2 \cdot \text{H}_2\text{O}]_2$, was prepared by reducing potassium dichromate with zinc and concentrated hydrochloric acid and running the filtered solution into a saturated solution of sodium acetate. $\text{CrCl}_2 \cdot 4\text{H}_2\text{O}$ was prepared by passing hydrogen chloride through a solution of chromium(II) acetate in concentrated hydro-

chloric acid cooled to 273 K. CrVO_4 was prepared as suggested by Brandt¹² by heating Cr_2O_3 and V_2O_5 at 1023 K for 24 h.

Al_2O_3 was prepared by the hydrolysis of analytical-reagent grade $\text{Al}(\text{NO}_3)_3$ with aqueous ammonia, drying the gel at 400 K for 24 h and calcining the sample at 800 K for 24 h. Chromia–alumina catalysts (5 and 10% by weight of chromia) were prepared by the impregnation method. Previously prepared Al_2O_3 was heated with the required amounts of $\text{Cr}(\text{NO}_3)_3$ solution and made into a slurry; the slurry was carefully evaporated to dryness and the sample was dried at 400 K, followed by calcination at 720 K for 24 h. Chromia–ZnO and chromia– SnO_2 samples (with 5 and 10% by weight of chromia) were prepared in a similar manner.

$\text{Cr}_{0.9}\text{Ru}_{0.1}\text{O}_2$ and $\text{Cr}_{0.6}\text{Ru}_{0.4}\text{O}_2$ were kindly supplied by Dr G. Demazeau of Laboratoire de Chimie du Solide du CNRS, Université de Bordeaux, France.

X-ray emission data collection

X-ray emission spectra were recorded on a 4 kW fluorescence spectrometer comprising a wide-angle horizontal goniometer by stepping the spectrometer through Bragg angle 2θ in steps of 0.01° . All the spectra were plotted by computer in order to reduce subjective and statistical bias. Energy was calibrated with respect to a chromium foil by assigning 5414.70 eV to the peak position of the $K\alpha_1$ line. The counting time during the step scanning was selected in such a way that the standard deviation in intensity measurement never exceeded 1%. It was 100 s for compounds and 500 s for catalysts, minerals and glassy materials using a tungsten tube operated at 50 kV and 50 mA. X-rays from this source are incident on the sample in the form of a solid disc obtained by compressing the powders of compounds and sometimes backing with terephthalic acid. The x-rays emitted from the sample were first collimated by Soller slits and then dispersed with a topaz crystal ($2d = 2.712 \text{ \AA}$). Photons were detected with a scintillation counter preceded by further collimation to reduce the background. The pulses from the detector were

amplified and counted using Harwell 2000 series electronics. The spectrometer was evacuated to 0.001 Torr (1 Torr = 133.3 Pa) by means of a rotary pump together with a liquid nitrogen cold trap for eliminating the air-scattering contribution to the background and for preventing the oxidation of compounds.

In order to confirm the reproducibility of the spectral features in tetravalent and hexavalent chromium compounds, five spectra each from two pellets of each sample were recorded. For divalent and trivalent compounds of chromium, several profiles of K α_1 and K α_2 were taken from at least five pellets prepared from each sample and all the spectra show the splitting or asymmetry in the emission lines. The samples used for this investigation were checked by taking their x-ray diffraction patterns on a Rigaku x-ray diffractometer before and after the measurements. No deterioration of the samples was detected before and after the measurements.

The spectrometer was housed in a dust-free air-conditioned room and all the measurements were carried out at a constant temperature maintained by ordinary air conditioners. The effect of temperature on the features of x-rays emission spectra was found to be negligible.

Data analysis

As the window width of the spectrometer varies with the wavelength and the exact shape of the window is not known,¹³ chromium spectra given in this work have not been corrected for the instrumental broadening. This is not considered to have any significant effect on the spectral interpretations which are offered. Moreover, these instrumental broadening corrections will not change the position of the emission line features and would have negligible effects on the other parameters of the emission line.

Peak positions and full widths at half maximum intensity (FWHM) were determined by fitting a Lorentzian function^{14,15} having a constant background to the experimental data. Fits were done in the energy range 5395–5425 eV. The function used for fitting is given by

$$I(E) = B + \frac{I_M}{1 + (E - E_M)^2/\Gamma^2} \quad (1)$$

where $I(E)$ is the intensity as a function of the energy, E , and is proportional to the observed number of counts, E_M is the peak energy of the emission line, Γ is its half-width and I_M its peak intensity and B is assumed to be a constant background.

Fits were made to each of the different experimental measurements and the parameters I_M , E_M , Γ , etc., were determined by minimizing the function χ^2 , given in Eqn (2), using the square root of the experimental value as a weighting factor for statistical errors:

$$\chi^2 = \sum_{i=1}^N \left\{ \frac{[I_i - I(E_i)]}{\sqrt{I_i}} \right\}^2 \quad (2)$$

where N is the number of data points in the particular run and I_i is the observed number of counts at the

energy E_i . The energy E_i of each data point was calculated in each run by matching the interpolated peak of the experimental data with the energy value tabulated for that line in Bearden's paper.¹⁶ We used the optimization program (BOTM algorithm) of Powell¹⁷ for performing the above calculations on an IBM PC-AT 486 computer with an Intel 80387 Math co-processor. The results of these numerical analyses for all the compounds except divalent and trivalent compounds are given in Table 1. For K α_1 and K α_2 lines of divalent and trivalent compounds asymmetry (or splitting) was not taken into account and the average profile was fitted to Eqn (1) and the results given in Table 1 for these compounds are for the average profiles of K α_1 and K α_2 . In fact, we can use the method of spectral deconvolution¹⁸ using Fourier transformation for resolving K α_1 (or K α_2) into two components, then fit the profile of each component to Eqn (1) and determine the line position, half-width and other parameters for each component more accurately. However, it requires a lot of computation and a large computer memory and time and therefore this analysis was not done.

The index of asymmetry of an x-ray emission line is defined by $(E_+ - E_M)/(E_M - E_-)$, where E_M is the energy of the peak and E_+ and E_- represent the energies of the half-intensity points on the low- and high-energy sides respectively. The indices for each emission line were determined from the raw x-ray emission data by using the above definition given by Allison.¹⁹ It should be noted that the relationship proposed by Sauder²⁰ was not employed for the calculations of the asymmetry indices in this investigation as it has rarely been used in the literature.

The energy positions of the spectral features have a probable error of ± 0.2 eV, but the energy difference could be measured to ± 0.1 eV or less. The half-widths have a probable error of ± 0.2 eV.

RESULTS AND DISCUSSION

In Figs 1–3 are shown typical x-ray K α emission spectra of chromium compounds, minerals, catalysts, coloured glass and oxide pigment. In Table 1 are given the results for the positions of K α_1 and K α_2 lines, their widths, asymmetry indices and their separations. In the following sections we discuss the results in greater detail.

Asymmetry indices

According to Allison,¹⁹ the index of asymmetry of an x-ray emission line is defined as the ratio of the part of the FWHM lying to the long-wavelength side of the maximum ordinate to that on the short-wavelength side. In Table 1 are given the results for the asymmetry of the K α_1 and K α_2 lines of chromium in chromium metal and in several model compounds as obtained in this investigation. It can be seen from Figs 1–3 and Table 1 that the K α_1 and K α_2 lines which are asym-

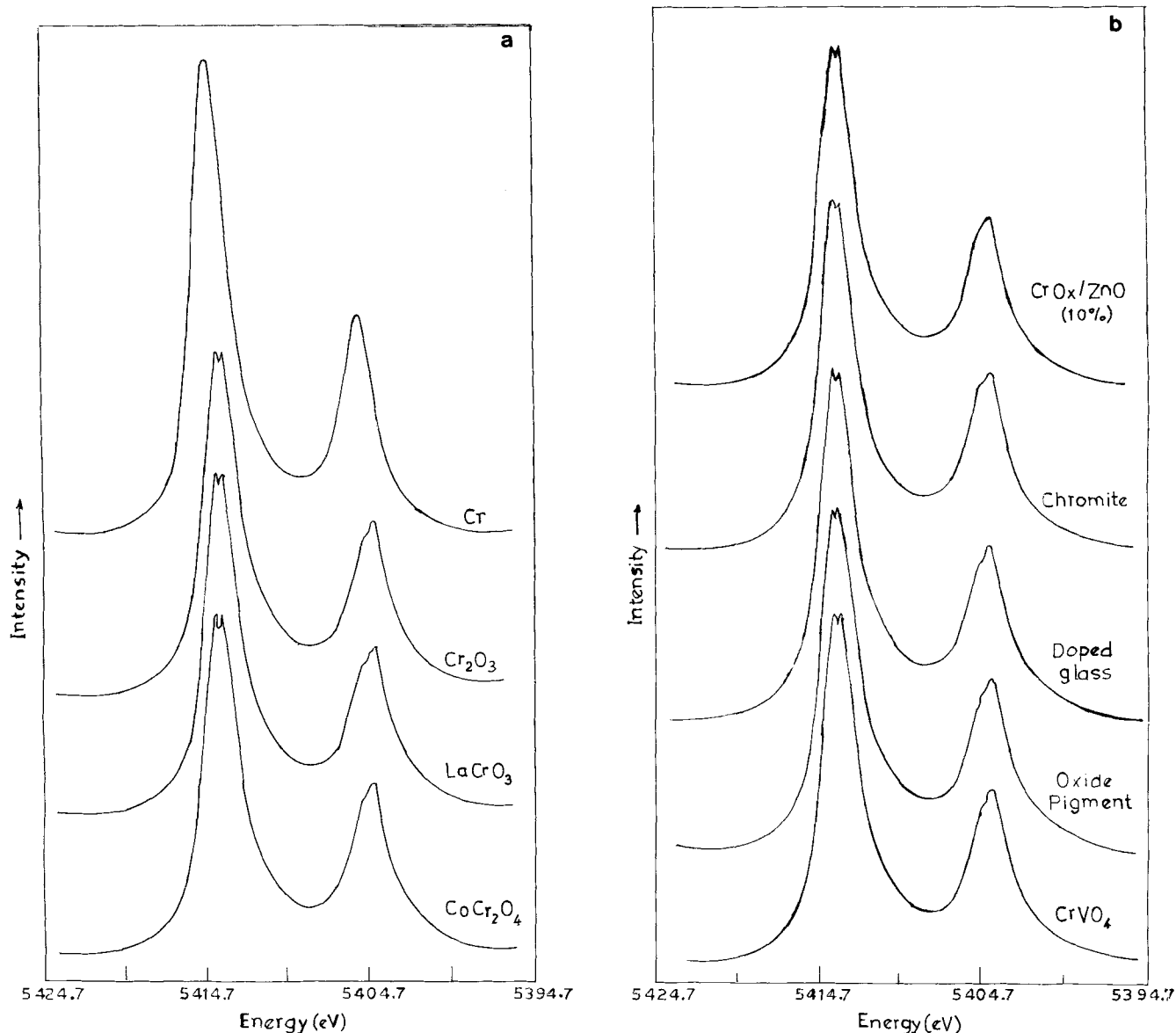


Figure 1. (a) $K\alpha_{1,2}$ lines of chromium metal, Cr_2O_3 , $LaCrO_3$ and $CoCr_2O_4$. (b) $K\alpha_{1,2}$ lines of 10% CrO_x -ZnO (reduced), chromite, doped glass, oxide pigment and $CrVO_4$.

metric in the case of chromium(II) chloride tetrahydrate and chromium(II) acetate (a dimer in which the chromium ion is in the 2+ valence state and is octahedrally coordinated²¹) and then gradually becomes more and more symmetric as the oxidation state of chromium increases. In K_2CrO_4 , Na_2CrO_4 , $(NH_4)_2Cr_2O_7$, CrO_3 and $NiCrO_4$, where chromium ions are in the hexavalent state, the emission lines are almost symmetric.

In the case of $Cr_{0.9}Ru_{0.1}O_2$, the values of the indices for both the $K\alpha_1$ and $K\alpha_2$ lines are of same order of magnitude as those obtained for tetravalent compounds such as CrO_2 , Ba_2CrO_4 and Sr_2CrO_4 . This implies that the chromium ion in $Cr_{0.9}Ru_{0.1}O_2$ exists in the 4+ valence state. However, the indices of the lines in $Cr_{0.6}Ru_{0.4}O_2$ are smaller than those measured for CrO_3 , $(NH_4)_2Cr_2O_7$, Na_2CrO_4 , $NiCrO_4$ and $K_2Cr_2O_7$, in which chromium exists in the hexavalent state, but it is greater than the value obtained for tetra-

valent chromium in CrO_2 , Ba_2CrO_4 and Sr_2CrO_4 . It would be appropriate to compare the indices with those for compounds in which chromium exists in the pentavalent state. As no pentavalent compounds were readily available, measurements could not be made on them. However, it is reasonable to say that the chromium ion in $Cr_{0.6}Ru_{0.4}O_2$ has an oxidation state higher than four but lower than six, i.e. the valency is 5+. Our findings in this respect are corroborated by the results of magnetic susceptibility measurements on these compounds by Demazeau *et al.*²²

In the chromite mineral obtained from Bairapur in the Hassan district of Karnataka, India, the values of the broadening indices determined from the x-ray emission lines are comparable to those of trivalent chromium compounds. The profiles of the $K\alpha_1$ and $K\alpha_2$ lines in this oxide material are indeed identical with those observed for $CoCr_2O_4$ and $MgCr_2O_4$. This is due

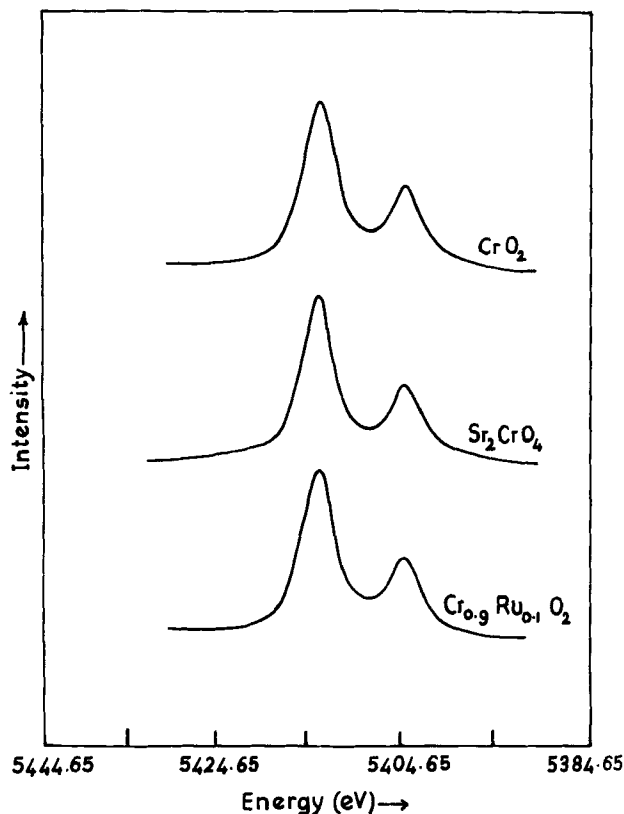


Figure 2. $K\alpha_{1,2}$ lines of CrO_2 , Sr_2CrO_4 and $\text{Cr}_{0.9}\text{Ru}_{0.1}\text{O}_2$.

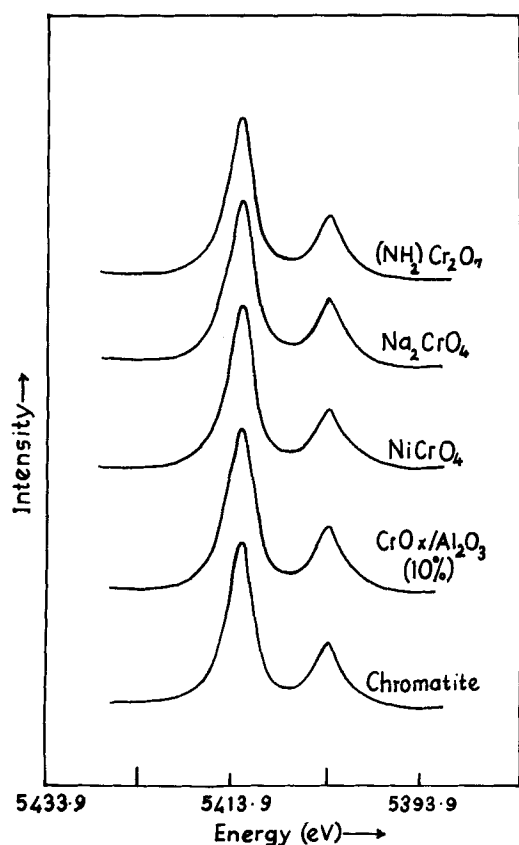


Figure 3. $K\alpha_{1,2}$ lines of $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$, Na_2CrO_4 , NiCrO_4 , 10% $\text{CrO}_x\text{-Al}_2\text{O}_3$ (calcined) and chromatite mineral.

to the fact that all three compounds have a spinel structure in which Cr^{3+} ions occupy octahedral sites.²³ The close similarity between the $K\alpha_{1,2}$ emission spectrum of chromatite mineral and the spectra of hexavalent chromium oxides suggests that the chromium ions are in the 6+ oxidation state in the mineral.²⁴

We studied the line shapes of chromium $K\alpha_1$ and $K\alpha_2$ emission lines in chromia catalysts supported on different substrates. We chose calcined and reduced $\text{CrO}_x\text{-Al}_2\text{O}_3$, reduced $\text{CrO}_x\text{-ZnO}$ and $\text{CrO}_x\text{-SnO}_2$ catalysts containing 5 and 10% by weight of chromia on the surface. Fig. 1(b) shows the profiles of lines in one of the catalysts containing 10% by weight of chromia on the surface after reduction with hydrogen at 720 K for 1 h. The $K\alpha$ signals are weak and therefore only the enlarged spectrum (in which all the intensities are multiplied by a factor of 10) is shown. The values of the indices in all the reduced chromia-ZnO and chromia-SnO₂ catalysts are almost the same. These values show close agreement with the values observed for trivalent chromium oxides. This means that chromium in these reduced samples is in the 3+ valence state. The chromia-alumina catalysts calcined at 720 K for 20 h show spectra (Fig. 3) similar to those of hexavalent chromium compounds and the emission spectra of reduced $\text{CrO}_x\text{-Al}_2\text{O}_3$ catalysts show a close similarity with those of trivalent chromium oxides. It is interesting that the XPS studies carried out²⁵ on chromium 2p bands of the reduced catalysts have shown the presence of Cr(III) and Cr(IV) species. However, the concentrations of the species which contains Cr(V) is very small. It is not possible to detect it in the x-ray emission spectra owing to the low intensity of the x-ray source used in this investigation. Perhaps with the intense radiation from a synchrotron or rotating anode x-ray generator it might be possible to detect such low-intensity signals.

We examined the emission spectra of chromium in a sample of coloured glass and an oxide pigment. We know that as chromium in such materials can have various oxidation states,²⁶ the determination of its oxidation state is very important for explaining the mechanism of colour development. The spectrum of soda-phosphate glass ($\text{Na}_2\text{O} \cdot 2\text{P}_2\text{O}_5$) doped with chromium oxide for making the glass coloured is shown in Fig. 1(b) together with the spectrum of the oxide pigment Victoria Green ($3\text{CaO} \cdot \text{Cr}_2\text{O}_3 \cdot 3\text{SiO}_2$). When these spectra are compared with the spectra of model chromium compounds, we find that they show similarity with the spectra of trivalent chromium compounds. The asymmetry parameters of $K\alpha_1$ and $K\alpha_2$ for these materials are also similar to those for Cr^{3+} compounds. The chromium ions in the coloured glass and Victoria Green pigment are therefore concluded to be in the trivalent state. Our observations that these materials contain Cr^{3+} ions is consistent with the results obtained on studies of absorption spectra of coloured glasses by Bates and Douglas²⁷ in the visible region and investigations on ceramic pigments by Evans.²⁸

In addition to the above observations, there is a definite correlation between the asymmetry indices and coordination number of the chromium ions in the materials studied in this investigation. For compounds in which the coordination number of chromium is high

Table 1. Energy shifts, half-widths, spin-orbit splittings and asymmetry indices of $K\alpha_1$ and $K\alpha_2$ emission lines in chromium compounds

Material	Q^a	ΔE^b (eV)		FWHM (eV)		δE^c (eV)	Asymmetry index	
		$K\alpha_1$	$K\alpha_2$	$K\alpha_1$	$K\alpha_2$		$K\alpha_1$	$K\alpha_2$
Cr metal	—	0.00 ^d (Ref.)	0.00 ^e (Ref.)	3.10	3.34	9.20	1.21	1.16
$[\text{Cr}(\text{OCOCH}_3)_2 \cdot \text{H}_2\text{O}]_2$	2+	+0.28	-0.32	4.75	5.23	9.80	1.36	1.32
$\text{CrCl}_2 \cdot 4\text{H}_2\text{O}$	2+	+0.30	-0.32	4.70	5.20	9.82	1.34	1.31
Cr_2O_3	3+	-0.05	-0.38	3.38	4.31	9.53	1.31	1.21
LaCrO_3	3+	-0.04	-0.35	4.00	4.30	9.51	1.30	1.22
MgCr_2O_4	3+	-0.03	-0.46	3.80	4.20	9.63	1.31	1.22
CoCr_2O_4	3+	-0.04	-0.36	3.90	4.21	9.52	1.31	1.21
CrO_2	4+	-0.06	-0.36	3.50	3.90	9.50	1.28	1.19
Sr_2CrO_4	4+	-0.09	-0.38	3.51	3.80	9.49	1.27	1.18
Ba_2CrO_4	4+	-0.05	-0.37	3.39	3.90	9.52	1.27	1.18
CrO_3	6+	-0.86	-0.96	2.90	3.90	9.30	1.14	1.10
$(\text{NH}_4)_2\text{Cr}_2\text{O}_7$	6+	-0.84	-0.94	2.80	3.91	9.30	1.14	1.11
$\text{K}_2\text{Cr}_2\text{O}_7$	6+	-0.80	-0.87	2.50	3.20	9.27	1.07	1.01
K_2CrO_4	6+	-0.82	-0.90	2.50	3.50	9.28	1.14	1.11
Na_2CrO_4	6+	-0.86	-0.94	2.61	3.40	9.28	1.14	1.10
NiCrO_4	6+	-0.83	-0.87	2.60	3.52	9.24	1.13	1.12
$\text{Cr}_{0.9}\text{Ru}_{0.1}\text{O}_2$	(4+)	-0.05	-0.36	3.51	3.90	9.51	1.28	1.19
$\text{Cr}_{0.6}\text{Ru}_{0.4}\text{O}_2$	(5+)	-0.32	-0.50	3.19	3.68	9.38	1.20	1.15
5% $\text{CrO}_x\text{-Al}_2\text{O}_3$ (calcined)	(6+)	-0.84	-0.96	2.89	3.90	9.32	1.14	1.11
10% $\text{CrO}_x\text{-Al}_2\text{O}_3$ (calcined)	(6+)	-0.80	-0.90	2.80	3.87	9.30	1.15	1.09
5% $\text{CrO}_x\text{-Al}_2\text{O}_3$ (reduced)	(3+)	-0.04	-0.35	3.70	4.20	9.51	1.29	1.21
10% $\text{CrO}_x\text{-Al}_2\text{O}_3$ (reduced)	(3+)	-0.03	-0.36	3.90	4.29	9.53	1.31	1.22
5% $\text{CrO}_x\text{-ZnO}$ (reduced)	(3+)	-0.05	-0.38	3.80	4.30	9.53	1.30	1.21
10% $\text{CrO}_x\text{-ZnO}$ (reduced)	(3+)	-0.04	-0.36	3.90	4.30	9.52	1.31	1.22
5% $\text{CrO}_x\text{-SnO}_2$ (reduced)	(3+)	-0.03	-0.38	3.80	4.21	9.53	1.30	1.20
10% $\text{CrO}_x\text{-SnO}_2$ (reduced)	(3+)	-0.04	-0.36	3.90	4.19	9.52	1.31	1.22
Doped soda-phosphate glass	(3+)	-0.04	-0.35	4.00	4.28	9.51	1.30	1.22
Victoria Green oxide pigment	(3+)	-0.05	-0.38	3.91	4.32	9.53	1.31	1.21
CrVO_4	(3+)	-0.04	-0.36	3.90	4.21	9.52	1.31	1.21
Chromite mineral	(3+)	-0.04	-0.36	3.90	4.20	9.52	1.31	1.21
Chromatite mineral	(6+)	-0.83	-0.87	2.60	3.50	9.24	1.13	1.11

^a Q = oxidation state.^b ΔE = energy shift.^c δE = energy separation between $K\alpha_1$ and $K\alpha_2$.^d Energy of the $K\alpha_1$ emission line = 5414.70 eV.^e Energy of the $K\alpha_2$ emission line = 5405.50 eV.

[e.g. in Cr_2O_3 , chromium(II) acetate, LaCrO_3 , CoCr_2O_4 , etc., the coordination number of chromium is six], asymmetry of the line is large. For a lower coordination of chromium ions in compounds such as CrO_3 , K_2CrO_4 and $\text{K}_2\text{Cr}_2\text{O}_7$ (where the coordination number of chromium ions is four), the emission line becomes more symmetric. This correlation can be employed to determine the coordination number of the metal ions in unknown materials. Thus, for example, the large values of the indices for $K\alpha_1$ and $K\alpha_2$ for 10% $\text{CrO}_x\text{-SnO}_2$ reduced catalyst and the small values of the indices in chromatite mineral suggest that the coordination numbers in these materials are six and four, respectively.

The observed reduction in the asymmetry indices with increase in oxidation state seems to be linked with number of unpaired 3d electrons of chromium. The more unpaired 3d electrons the atom possesses, the more asymmetric will be the line observed. This kind of observation led Tsutsumi and co-workers^{7,8} to consider that the interaction between the hole created in the

$2p_{3/2}$ or $2p_{1/2}$ shell (due to the transition of an electron from this shell to the 1s level) and the electrons in the incomplete 3d shell in the transition metal atoms is responsible for asymmetric nature of $K\alpha_{1,2}$ lines. They proposed a theoretical model based on this idea to account for the asymmetry in the x-ray emission lines in the first-row transition metal compounds. However, this is not the only consideration which can explain the origin of the asymmetry of the line; there are other considerations which are based on the relaxation effect of the inner state proposed by Parratt²⁹ or on the interactions between 2p hole and electrons in the Fermi sea as proposed by Doniach and Sunjic.³⁰

Full widths at half maximum intensity

The FWHM values for all the compounds investigated are given in Table 1. For chromium metal, the FWHM values for $K\alpha_1$ and $K\alpha_2$ emission lines are 3.1 and 3.34

eV, respectively. Both the $K\alpha_1$ and $K\alpha_2$ lines become broad when the metal forms chemical compounds. Among all the compounds, the divalent chromium(II) acetate shows large widths for both lines. However, when the oxidation state increases, the lines become more and more narrow and accordingly the width decreases. In all the hexavalent compounds the lines are very sharp and the widths of these lines are very small. These findings on FWHM values for model compounds can now be used to characterize the samples of catalysts, minerals and other materials. As can be seen from Table 1, the widths of the $K\alpha_1$ and $K\alpha_2$ lines in the chromite mineral, $\text{CrO}_x\text{-ZnO}$, $\text{CrO}_x\text{-SnO}_2$ catalysts, doped soda-phosphate glass and oxide pigment suggest the presence of Cr^{3+} ions in these materials. On the other hand, the same order of magnitudes of the widths of the emission lines in the $\text{CrO}_x\text{-Al}_2\text{O}_3$ calcined catalysts, chromatite mineral and those in hexavalent compounds is indicative of the existence of Cr^{6+} ions in these compounds. Thus, like asymmetry parameters, the widths of emission lines can also be used to identify the oxidation states in compounds for which they are unknown.

Spin-orbit splitting

It is well known³¹ that the energy difference between $K\alpha_1$ ($2p_{3/2} \rightarrow 1s$) and $K\alpha_2$ ($2p_{1/2} \rightarrow 1s$) lines gives the values of spin-orbit splitting. This corresponds to the difference in energy between $2p_{3/2}$ and $2p_{1/2}$ core levels as the initial level involved in the transition ($1s$) is the same for both lines. In x-ray spectroscopic notation,³¹ it is denoted by the $L_{II}\text{-}L_{III}$ doublet interval. In Table 1, the $L_{II}\text{-}L_{III}$ separations obtained from x-ray emission measurements are given. For chromium metal, the value of spin-orbit splitting observed is 9.2 eV. In the case of the materials examined, although the variation in the values of this energy separation is relatively small, there is a definite change in its value with increase in the oxidation state (except for tetravalent compounds). In the divalent chromium(II) acetate it is maximum at 9.8 eV and it decreases with increase in the oxidation state of chromium. It is minimum in the hexavalent chromium compounds. In the case of minerals, catalysts, coloured glasses and oxide pigment, in which the oxidation states of metal ions are usually unknown, data from Table 1 on energy separations can be employed to extract information about the valence states. Thus, for example, the value of the spin-orbit splitting in the coloured glass is close to that observed in the trivalent compounds of chromium, suggesting that the sample of coloured glass contains Cr^{3+} ions.

It should be noted that the tetravalent compounds show the same energy separation as those in trivalent compounds. Careful x-ray diffraction analysis of tetravalent compounds showed no extra lines in the diffraction pattern, and this rules out any possibility of impurities. The same values of energy separations between tetravalent and trivalent compounds may be due to the solid-state effects which can affect the energy levels in the tetravalent compounds, as has been discussed by Kim and Winograd³² and Ikemoto *et al.*³³

Even in the XPS of Cr^{4+} compounds reported by Okamoto *et al.*³⁴ and Cumino and co-workers,^{35,36} the values of the spin-orbit splitting observed are similar to those in Cr^{3+} compounds. Excluding the tetravalent compounds, it is clearly seen from Table 1 that Cr^{6+} , Cr^{3+} , Cr^{2+} and Cr metal can be distinguished by the energy separation between the $K\alpha_1$ and $K\alpha_2$ emission lines. If we want to make use of tetravalent compounds as models for the analysis of the spectra of unknown materials, we should use the asymmetry parameters and widths of the lines and not the spin-orbit splittings for identification of valence states.

Chemical shifts

As has been mentioned, apart from the modifications to the width and shape of $K\alpha_1$ and $K\alpha_2$ lines when the environment of the emitting atom is changed, there are changes in the position of emission lines with respect to those in the pure metal. These changes are called chemical shifts. The values of these shifts measured in the compounds are summarized in Table 1. The shifts are towards the low-energy side except for divalent compounds for which the shift of the $K\alpha_1$ line is towards the high-energy side. A trend is clearly seen between oxidation states and Cr $K\alpha_{1,2}$ line shifts (here also similarly to the results on spin-orbit splitting, the shifts in tetravalent compounds are close to those in trivalent compounds). The magnitude of these energy shifts (excluding the shifts in tetravalent compounds) increases with increase in the oxidation state. Although the distribution within trivalent or hexavalent compounds may cause some ambiguity, the separations between the shifts among different oxidation states are large enough to be distinguished. Leonhardt and Meisel² reported that complex materials show different shifts for normal compounds, even when chromium has the same formal oxidation state. The effect of electronegativity, the nature of the ligands and the distribution of ligands around the central emitting atoms are some of the factors which may cause this variation. We consider, however, that with certain restrictions, a good correlation can be established between the shifts and the oxidation states. The restriction is that the bonding ligands to the emitting atom should be the same. If we want to include the other ligands, we should take into account the factors mentioned above. As can be seen from Table 1 the bonding ligand being the same in all the compounds investigated in this work [except chromium(II) chloride], the correlation between Cr $K\alpha_{1,2}$ line shifts and oxidation states is excellent.

Having found a correlation between chemical shift and oxidation state, we can, in principle, determine unknown oxidation states in various materials. For chromia-ZnO and chromia-SnO₂ catalysts, the data on chemical shift show the presence of Cr^{3+} ions. In chromite and chromatite minerals, it is evident from the values of their line shifts that they contain Cr^{3+} and Cr^{6+} ions, respectively. Hence the chemical shift of the emission line, similarly to asymmetry index, width and spin-orbit splitting, is also an important factor in the characterization of the materials.

Finally, we shall discuss our results on CrVO_4 . It is specifically considered here because the valence states of chromium and vanadium in this material have been in doubt. We cannot obtain any idea about the valence states from x-ray diffraction results since Cr and V have almost identical x-ray scattering powers. The composition of this compound was first reported by Brandt.¹² The formula CrVO_4 was deduced from consideration of ionic radii. Wyckoff²³ used the compound as a structure type (written as VCrO_4) and cited only the reference of Brandt. Neutron diffraction and magnetic susceptibility measurements³⁶⁻³⁸ were carried out on this compound to establish the formal oxidation state of the cations. According to these studies the orthorhombic $Cmcm$ structure for this compound is unique; it consists of CrO_6 edge-shared octahedra as in the rutile structure, but these chains are interconnected through vertices of VO_4 tetrahedra. This arrangement indicates the formation of $\text{Cr}^{3+}\text{V}^{5+}\text{O}_4$ and not $\text{Cr}^{4+}\text{V}^{4+}\text{O}_4$. To see whether we obtain the same information from x-ray emission spectra, we examined its spectrum and compared it with the spectra of Cr_2O_3 , CrO_2 and NiCrO_4 . The profiles of the $K\alpha_1$ and $K\alpha_2$ lines are shown in Fig. 1(b). It is observed that the profiles of these lines are different from those in NiCrO_4 (Fig. 3), but similar to those in Cr_2O_3 [Fig. 1(a)]. The values of the broadening indices, widths, spin-orbit splittings and chemical shifts are also similar to those observed for trivalent chro-

mium compounds. Hence all the features of the emission spectrum of CrVO_4 show that the chromium ions in this compound are in the $3+$ state. In this respect, our results support the conclusions drawn from neutron diffraction and magnetic susceptibility studies.

CONCLUSIONS

We have presented and discussed the essential features of the $K\alpha_1$ and $K\alpha_2$ emission lines of chromium ions for selected materials. The observed spectral features, namely the asymmetry indices, FWHM values, chemical shifts and energy separations between $K\alpha_1$ and $K\alpha_2$ lines, show interesting correlations with formal oxidation states. By comparing the spectral features of minerals, catalysts, coloured glass and oxide pigment with those of model compounds, formal oxidation states of chromium ions in these materials have been determined.

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