The Origin of the $K\beta'$ Satellite Peak in the X-Ray Fluorescence Spectra of Iron Compounds: a Correlation with Magnetic Susceptibility

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Summary The presence or absence of a low energy $K\beta'$ satellite peak in the X-ray fluorescence spectra of iron compounds is correlated with a high or a low spin state of the iron atom.

THE X-ray emission spectra of eight iron compounds were recorded (*ca.* 7000 e.v.) using a Philips 1410 XRF spectrometer with a germanium crystal ($2d = 0{\cdot}655$ nm). Third order diffraction was observed so as to obtain good resolution. Typical results are shown in the Figure. The compounds studied obviously fall into two classes, those that do, and those that do not exhibit a $K\beta'$ peak of somewhat lower energy than the main $K\beta_{1,3}$ peak ($3p - 1s$ transition). The data presented in the Table show that the presence or absence of this satellite peak can be correlated with the spin state of the iron atom in the complex and not with the formal valence of the ion.

This correlation is reasonable since spin–orbit coupling between a partially filled $3d$ shell and a vacancy in the $3p$ shell is inevitable. Exchange interaction has also been proposed[1] as the cause of the $K\beta'$ satellite observed in the X-ray emission spectra of other paramagnetic transition metal compounds.

The final state of the iron atom after the emission of the X-ray photon is the same as that which would be observed in an X-ray photoelectron experiment. Fadley and Shirley[2] have studied two relevant species; high-spin FeF_3 and low-spin $[Fe(CN)_6]^{4-}$. In the former case they report peaks corresponding to three different energy states—for

TABLE

Compound	Valence state iron	μ_{eff} (300 K) B.M.	$K\beta' : K\beta_{1,3}$ intensity ratio %	$K\beta$ spectrum type (Figure)
$Fe(C_6H_5)_2$	2	0	<5	(i)
$K_4[Fe(CN)_6]$	2	0	<5	(i)
$K_3[Fe(CN)_6]$	3	2·25	<5	(i)
$K_2SO_4 \cdot FeSO_4 \cdot 6H_2O$	2	(5·22)[a]	22	(iii)
$K_2SO_4 \cdot Fe_2(SO_4)_3 \cdot 2H_2O$	3	(5·95)[b]	28	(iii)
$K_3[Fe(C_2O_4)_3] \cdot 3H_2O$	3	5·90	25	(iii)
$Fe_2(SO_4)_3$	3	(5·95)[b]	30	(iii)
Fe_2O_3	3	variable	30	(ii)

[a] Data for $FeSO_4,7H_2O$. [b] Data for $FeCl_3,6H_2O$.

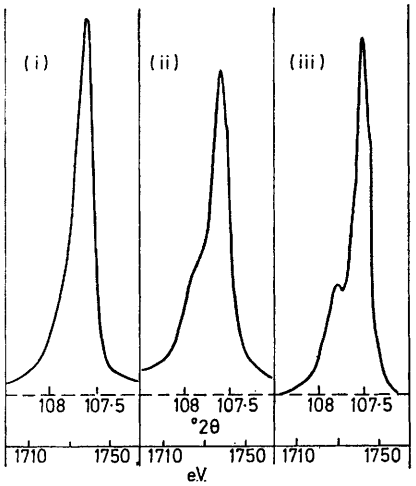

FIGURE. *Kβ emission spectra for (i) ferrocene, (ii) ferric oxide, and (iii) ferrous alum.*

the latter only one peak was observed. These experimental results would seem to provide confirmation of the hypothesis advanced above.

If this explanation is correct this technique might provide a unique way of determining the local spin-state of an atom in a complex. In simple complexes there is no problem because the bulk magnetic susceptibility gives a reasonable indication. But in more complex molecules long-range spin coupling can reduce the paramagnetic susceptibility. Since *X*-ray emission spectroscopy probes the electronic environment of an individual atom such cooperative effects might not be observed.

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