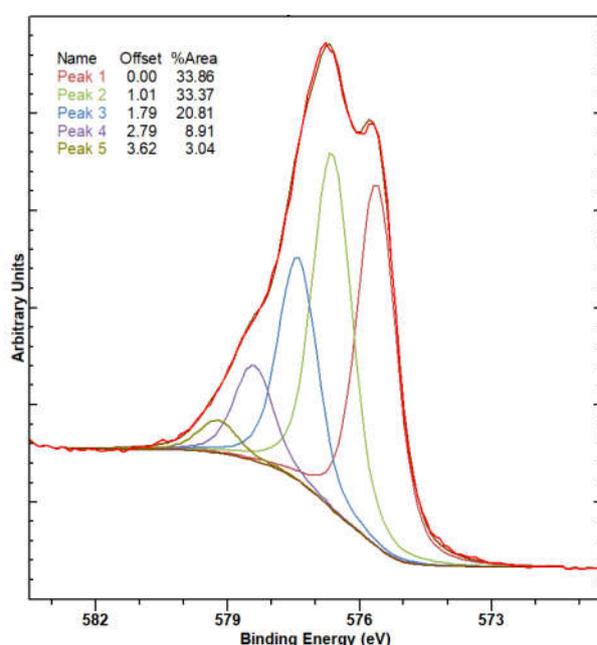


### Theory

Multiplet splitting occurs when an emitting atom contains unpaired electrons, such an example is Cr(III), which has the electronic configuration  $3p^6 3d^3$ .

When a core-hole vacancy is created through photoemission, there can be coupling between the unpaired electron in the core and unpaired electrons in the outer shell. This coupling can give rise to several final states, such as that observed in chromium (III) oxide,  $\text{Cr}_2\text{O}_3$  (figure 1), which appear as a multiple-peak envelope [1]. The presence of multiple peaks can often be misinterpreted as differing oxidation states and therefore lead to erroneous interpretations of data.



**Figure 1.**  $\text{Cr}(2p_{3/2})$  spectrum for a  $\text{Cr}_2\text{O}_3$  powder sample showing the multiplet splitting, together with peak offsets from the primary peak

Since valence electrons are involved in bonding, they are crucial in determining multiplet splitting as it becomes sensitive to the local chemical environment and also explains why multiplet splitting can be both paramagnetic and diamagnetic species (for example  $\text{Co(II)}$  and  $\text{Co(III)}$ ).

### Understanding the Shapes of Multiplet Structure

The ideal starting point to understand multiplet structure, shapes and number of peaks is that of Gupta and Sen [2], whose early Hartree-Fock (HF) calculations showed graphically the multiplet structure of core  $p$ -valence levels of free ion state first row transition metals.

Whilst important in gaining an understanding of the multiplet structures, these HF calculations are for free ion states, and therefore in transition metals and associated compounds, may be influenced by charge-transfer from ligands that may change the spacing and intensity of such peaks.

That said, these relative changes can be utilized for transition metal compounds to differentiate between species which more closely approximating free ions from those in which charge transfer from the bonded neighbouring ions may have changed both the effective oxidation state and multiplet splitting of the core transition metal. Such an example of this change in local electronic structure has been used to explain the differences between the observed Ni(2p) spectra of nickel oxide and its oxy/hydroxides [3]

### What Exhibits Multiplet Splitting?

For ease of reference, table 1 (page 3) provides a summary of the first-row transition metal species which exhibit multiplet splitting.

For Sc, Ti, V, Cu and Zn species, multiplet splitting is not present (or if present, is not well resolved and typically manifests as peak broadening [4]), whereas Cr, Fe, Mn, Co and Ni species show significant multiplet splitting [5].

### Further Reading

For those wishing to explore multiplet splitting further, we recommend the following texts:

- F. de Groot, A. Kotani, Core Level Spectroscopy of Solids, CRC Press, Boca Raton, 2008.
- P. van der Heide, X-ray Photoelectron Spectroscopy: An introduction to Principles and Practices, John Wiley & Sons, 2011

### References

[1] J.F. Moulder, W.F. Stickle, P.E. Sobol, K.D. Bomben, Handbook of X-ray Photoelectron Spectroscopy, Perkin-Elmer Corp, Eden Prairie, MN, 1992.

[2] R.P. Gupta, S.K. Sen, Phys. Rev. B 12 (1975) 15.

[3] A.P. Grosvenor, M.C. Biesinger, R.St.C. Smart, N.S. McIntyre, Surf. Sci. 600 (2006) 1771.

[4] M.C. Biesinger, L.W.M. Lau, A.R. Gerson, R.St.C. Smart, Appl. Surf. Sci. 257 (2010) 887.

[5] M.C. Biesinger, B.P. Payne, A.P. Grosvenor, L.W.M. Lau, A.R. Gerson, R.St.C. Smart, Appl. Surf. Sci. 257 (2011) 2717.

# Technical Note #3

## Multiplet Splitting



harwellxps

Elektronen Konfiguration	[Ar]	[Ar] 3d <sup>1</sup>	[Ar] 3d <sup>2</sup>	[Ar] 3d <sup>3</sup>	[Ar] 3d <sup>1</sup> 4s <sup>2</sup>	[Ar] 3d <sup>4</sup>	[Ar] 3d <sup>2</sup> 4s <sup>2</sup>	[Ar] 3d <sup>5</sup>	[Ar] 3d <sup>3</sup> 4s <sup>2</sup>	[Ar] 3d <sup>6</sup>	[Ar] 3d <sup>5</sup> 4s <sup>1</sup>	[Ar] 3d <sup>7</sup>	[Ar] 3d <sup>5</sup> 4s <sup>2</sup>	[Ar] 3d <sup>8</sup>	[Ar] 3d <sup>6</sup> 4s <sup>2</sup>	[Ar] 3d <sup>9</sup>	[Ar] 3d <sup>7</sup> 4s <sup>2</sup>	[Ar] 3d <sup>10</sup>	[Ar] 3d <sup>8</sup> 4s <sup>2</sup>	[Ar] 3d <sup>10</sup> 4s <sup>1</sup>	[Ar] 3d <sup>10</sup> 4s <sup>2</sup>	
Sc	Sc(III)				Sc(0)																	
Ti	Ti(IV)	Ti(III)	Ti(II)			Ti(0)																
V	V(V)	V(IV)	V(III)	V(II)				V(0)														
Cr	Cr(VI)		Cr(IV)	Cr(III)		Cr(II)			Cr(0)													
Mn	Mn(VII)	Mn(VI)		Mn(IV)		Mn(III)		Mn(II)				Mn(0)										
Fe								Fe(III)		Fe(II)				Fe(0)								
Co									Co(III)		Co(II)					Co(0)						
Ni											Ni(III)		Ni(II)							Ni(0)		
Cu														Cu(II)			Cu(I)			Cu(0)		
Zn																	Zn(II)					Zn(0)

Code:

	No Multiplet Splitting
	Multiplet Splitting Present but not Well Resolved (e.g. Peak Broadening)
	Multiplet Splitting Resolved in XPS Spectra

**Table 1.** First row transition metal species that show multiplet splitting in their XPS spectra.

Note, the information presented is for high spin compounds. For low spin Fe(II) and Ni(II) species, the electrons are paired and no multiplet splitting is observed.