

COVALENCY IN FLUORIDE PEROVSKITES

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In $[\text{MF}_6]^{n-}$ complexes, F^- ions permit us to measure and calculate covalency parameters through the superhyperfine interaction. In octahedral complexes the superhyperfine parameters $A_{//}$ and A_{\perp} are related to the transferred spin densities f_s , f_{σ} , f_{π} by:

$$A_{//} = 49.6 R^{-3} + 172 (f_{\sigma} - f_{\pi}) + 3.10^3 f_s; \quad A_{\perp} = 24R^{-3} - 86(f_{\sigma} - f_{\pi}) + 3.10^3 f_s$$

The transferred spin densities are related to the covalency parameters

$$f_{\pi} = \frac{1}{4} (N_{t_{2g}} \lambda_{\pi})^2 f_{\sigma} = \frac{1}{3} (N_{e_g} \lambda_{\sigma})^2 f_s = \frac{1}{3} (N_{e_g} \lambda_s)^2$$

where $N_i \lambda_i$ are defined through the antibonding orbitals :

$$\psi_{t_{2g}} = N_{t_{2g}} (\varphi_{t_{2g}} - \lambda_{\pi} \psi_{2p\pi}) \quad \psi_{e_g} = N_{e_g} (\varphi_{e_g} - \lambda_{\sigma} \psi_{2p\sigma} - \lambda_s \psi_{2s})$$

associated to the valence electrons. φ_i are (3d) metal orbitals, and the index i holds for the symmetry t_{2g} or e_g . ψ_i are linear combinations of 2s and 2p orbitals. In reference [1] one presents our model. In table 1 one gives general results about covalency for (3d)ⁿ metal ions : V^{2+} , Cr^{3+} , Ni^{2+} , Mn^{2+} , Fe^{3+} .

In reference 2 the results for different metal ligand distances are given for V^{2+} and Cr^{3+} . The calculated value $f_{\sigma} - f_{\pi}$ nearly varies as R^{-3} . We may notice that a law as R^{-3} permits us to calibrate R easily with the experimental anisotropic S.H.F. interaction since the dipole interaction varies as R^{-3} . For (3d)⁵ ions, the more surprising result is the increase of f_{σ} and f_{π} with R, for $[\text{FeF}_6]^{3-}$ complexes (Ref. 4), at such a rate that for $R > 1.9 \text{ \AA}$ the ionic approximation is not consistent with the calculated value of f_{σ} .

In KZnF_3 , the impurity which has a larger ionic radius than Zn^{2+} nearly would act as a hard sphere and would repel the nearest ligand. Conversely in the compact RbCdF_3 lattice, the inward relaxation tends to a nearly compact

Table 1 : Experimental (B) and calculated values (A) of spin densities.
 f_i' reveal polarization mechanism on F^- ions.

Conf.	Bond	f_B		f_B'		f_O		f_O'		f_V		f_V'		Ref.
		A	B	A	B	A	B	A	B	A	B	A	B	
$(t_{2g})^3$ [1,2]	$V^{2+} F^-$ 2.00 Å	0		-0.02	-0.1	0		-0.38	-0.3	2.6	2.6	-2.98	-3.1	[5]
	$Cr^{3+} F^-$ 1.9 Å	0		-0.02		0		-0.3		4.4	4.	-4.52	-4.9	[6,7]
$(t_{2g})^6(e_g)^2$ [3]	$Mn^{2+} F^-$ 2.00 Å	0.3	0.57	0	0	3.61	3.72	0	0	0	0	3.61	3.72	[8,9]
				0	0	[3]		0	0	0	0			
$(t_{2g})^3(e_g)^2$ [4]	$Mn^{2+} F^-$ 2.00 Å	0.78	0.52			2.8				2.4		0.4	0.3	[10,11, 12]
	$Fe^{3+} F^-$ 1.9 Å	0.88	0.78			1.08				7.4		3.4	3.5	[12,13]
						[4]				[4]		[5]		

arrangement of the ligands around the small impurity. In $KZnF_3 : Fe^{3+}$ we have chosen $R = 1.9$ Å, i.e. a rather strong inward relaxation favoured by the small ionic radius and the extra positive charge of Fe^{3+} . One finds a good agreement between theory and experiments.

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