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LETTER TO THE EDITOR

Covalency in NiF$_6^{5-}$: the Jahn–Teller centre in LiF:Ni$^+$ revisited

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Abstract. Self-consistent charge extended Hückel (SCCEH) and MS X$_\alpha$ calculations performed for several metal–ligand distances have been carried out in order to investigate the superhyperfine (SHF) tensor of 'compressed' and 'elongated' NiF$_6^{5-}$ complexes in LiF. The SCCEH (made for clusters involving up to 81 ions) and the MS X$_\alpha$ calculations (made for the NiLi$_{12}$F$_{14}^-$ cluster) *both* support the idea that the VII centre in LiF:Ni$^+$ can hardly be assigned to a pure Jahn–Teller centre (without any close defect) with compressed geometry, while the experimental SHF tensor of elongated NiF$_6^{5-}$ species is reasonably accounted for. Also *both* types of calculation indicate that for the compressed NiF$_6^{5-}$ complexes f_σ(AX) can increase upon increasing the distance between Ni$^+$ and axial ligands.

The Ni$^+$ centre in LiF termed as VII [1] has been considered as a genuine example of a *pure* Jahn–Teller system in which the dynamic effects associated with the zero-point motion, firstly discussed by O'Brien [2], are observed [3]. The VII centre was supposed to consist of *compressed* NiF$_6^{5-}$ units in which the 3d^9 ion, Ni$^+$, is surrounded by two nearest 'axial' F$^-$ ligands at a distance R_{AX} and by four further 'equatorial' F$^-$ ligands lying at R_{EQ} from Ni$^+$ (figure 1). In this static situation the unpaired electron lies in an antibonding a$_{1g}^*$ orbital whose wavefunction transforms as $3z^2 - r^2$.

Assuming this model for the VII centre, the experimental value $g_\parallel - g_0 = 0.063$ reported by Hayes and Wilkens [1] cannot be explained within a crystal-field scheme which predicts a negative $g_\parallel$-shift [3]. In a more realistic molecular orbital description of the D$_{4h}$ compressed NiF$_6^{5-}$ unit, positive contributions to the $g_\parallel$-shift can, however, be found [4]. Nevertheless this contribution to the $g_\parallel$-shift arising from the charge transfer a$_{2g} \rightarrow$ a$_{1g}^*$ excitation amounts only to less than $+5 \times 10^{-3}$ for the present case. This small positive contribution is due in part to the fact that charge transfer excitations for NiF$_6^{5-}$ units lie in the vacuum ultraviolet region [5, 6].

The 'anomalous' positive $g_\parallel$-shift of the VII centre in LiF:Ni$^+$ has been explained [2, 3] on the basis of dynamic effects associated with a true Jahn–Teller system. In fact, when in an octahedral geometry an E$_g$ orbital electronic state is coupled to an ε_g vibration mode (defined by the normal coordinates $Q_2 = \rho \sin \theta$ and $Q_3 = \rho \cos \theta$ [2, 3]) the lowest adiabatic electronic wavefunction, $|\Psi(\theta)\rangle$, is given by

$$|\Psi(\theta)\rangle = \cos(\theta/2)|x^2 - y^2\rangle + \sin(\theta/2)|3z^2 - r^2\rangle \tag{1}$$

where $|x^2 - y^2\rangle$ and $|3z^2 - r^2\rangle$ mean the two wavefunctions of the E$_g$ doublet transforming as $x^2 - y^2$ and $3z^2 - r^2$, respectively. Equation (1) then points out that the
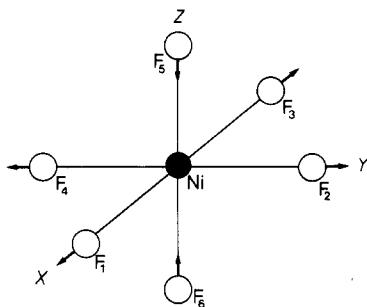
Figure 1. Arrangement of the six nearest F^- ions around a Ni^+ impurity in a cubic fluoride material. The figure depicts a 'compressed' situation.

instantaneous local symmetry around the metallic cation is orthorhombic in the neighbourhood of the minima, appearing at $\theta = 2\pi/6$; π; $5\pi/3$ for a compressed situation. This circumstance allows the admixture of $|x^2 - y^2\rangle$ and $|3z^2 - r^2\rangle$ in the adiabatic wavefunction $|\Psi(\theta)\rangle$. Therefore if the interaction between the three equivalent minima is suppressed by the random strains [7] the EPR spectrum can obey a D_{4h} geometry and the excursions on θ values in equation (1) close to the minima due to zero-point vibrations give [2]

$$g_\| = \overline{\cos^2(\theta/2)}\, g_\|(x^2 - y^2) + \overline{\sin^2(\theta/2)}\, g_\|(3z^2 - r^2). \tag{2}$$

As $g_\|(x^2 - y^2)$ for a ground state of type $x^2 - y^2$ is higher than g_0 [3], the experimental $\overline{g_\| - g_0} = 0.063$ value for the VII centre was explained on the basis of equation (2) with $\overline{\sin^2(\theta/2)} = 0.9$.

Nevertheless the experimental superhyperfine (SHF) tensor (described by the usual $T_\| = A_s + 2A_\sigma$; $T_\perp = A_s - A_\sigma$ components) corresponding to the two axial ligands of the VII centre is in fact quite different from that found for Ni^+ centres with elongated geometry and where the unpaired electron lies in an approximately $x^2 - y^2$ type orbital. In fact $A_\sigma(AX) = (47 \pm 1) \times 10^{-4}\,cm^{-1}$ for the axial ligands of the VII centre [1] while $A_\sigma(EQ) \simeq 13 \times 10^{-4}\,cm^{-1}$ for the NiF_6^{5-} centres with elongated O_h geometry recently found in several fluoroperovskites [8–10]. This geometry was also assumed for the so-called I centre in LiF: Ni^+ which exhibits a value $A_\sigma(EQ) = (12.5 \pm 1) \times 10^{-4}\,cm^{-1}$ [1].

As far as we know this significant difference between the experimental A_σ values of the elongated NiF_6^{5-} units and that for the VII centre in LiF has not been analysed in detail. However it could provide us with significant arguments for supporting or rejecting the proposed model for the VII centre.

Owing to this fact we have calculated theoretically A_σ and A_s for the static elongated and compressed NiF_6^{5-} complexes in LiF. The most relevant characteristics of our calculations are as follows:

(i) two different methods are used; the self-consistent charge extended Hückel (SCCEH) as well as the MS X_α;

(ii) in the case of the SCCEH method, calculations are carried out for clusters around Ni^+ impurities of different sizes. The total number, N, of ions included in the cluster is $N = 7$ (NiF_6^{5-}), $N = 27$ ($NiLi_{12}F_{14}^-$) and $N = 81$ ($NiLi_{42}F_{38}^{5+}$). The MS X_α method is only carried out for $N = 27$;

(iii) calculations are performed for different values of the metal–ligand distances R_{EQ} and R_{AX}. The position of other ions lying further from Ni^+ is assumed to be the same as for pure LiF.

The semi-empirical SCCEH method has the advantage of taking the diagonal matrix elements of the one-electron hamiltonian, h, from atomic experimental results. Methods

of this kind are currently used for metal clusters [11] as well as in the realm of pure and doped non-metallic solids [12–16]. In the present case the diagonal elements h_{nn} are taken as

$$h_{nn} = -\text{VSIE}(q) + V_M + V_W. \tag{3}$$

Here, VSIE (q) depends on the type of orbital and on the total charge of the atom and is derived from atomic data [17, 18]. V_M denotes the electrostatic interaction between an electron in an atomic orbital n and the non-zero net charges of *other* atoms in the cluster of N atoms. Finally, V_W corresponds to the electrostatic interaction between the electrons in the cluster and ions lying outside, described by a Watson sphere. The non-diagonal matrix elements have been calculated using the expression in [19] and Clementi–Roetti wavefunctions [18] for computing the overlap integrals. More details are given in [6]. A calculation for $N = 81$ and one set of metal–ligand distances requires a CPU time of about 17 hours on a VAX 8350 computer.

The standard version of the SCF MS X_α method [20] is used to perform a spin-restricted calculation on a cluster of 27 atoms centred around the nickel. In the initial atomic calculations, performed to construct the starting molecular potential, neutral atoms have been used. The SCF procedure was stopped when the relative change in the potential was 10^{-3} or smaller. The ratios of the sphere radii were fixed to the values obtained using the Norman procedure [21]. We allow the atomic spheres to overlap, the absolute values of the sphere radii being determined by imposing the condition that the virial ratio $-2\langle T \rangle/\langle V \rangle$ be *exactly* one. The outer sphere was tangential to the more external fluoride spheres, and the -1 charge of the cluster was stabilised using a Watson sphere of opposite charge with the same radius as the outer sphere. The CPU time required for $N = 27$ and a given choice of R_{AX}, R_{EQ} and of the radii of atomic spheres is about 5 hours on a VAX 8350 computer.

The calculated wavefunctions of the NiF$_6^{5-}$ unit embedded in the cluster with N ions and called ψ_a or ψ_b (for elongated and compressed situations respectively) can be described in a compact form as follows

$$|\psi_\alpha\rangle = N_\alpha\Bigg(|\varphi_{M,\alpha}\rangle - \sum_{i=1}^{2} \lambda^i_{p\sigma,\alpha}|\chi^i_{p\sigma,\alpha}\rangle$$
$$- \sum_{i=1}^{2} \lambda^i_{s,\alpha}|\chi^i_{s,\alpha}\rangle\Bigg) + |\varphi_{R,\alpha}\rangle \qquad \alpha = a; b. \tag{4}$$

The first term denotes a molecular orbital of the distorted NiF$_6^{5-}$ complex while $|\varphi_{R,\alpha}\rangle$ is the contribution arising from orbitals centred on further ions in the N-ion cluster. The indexes $i = 1$ and $i = 2$ refer to axial and equatorial ligands respectively. Let us now specify the meaning of $|\varphi_{M,\alpha}\rangle$, $|\chi^2_{p\sigma,\alpha}\rangle$, and so on in equation (4) for the wavefunction corresponding to the unpaired electron. Taking as a guide $|\chi^1_{p\sigma,b}\rangle$ and $|\chi^2_{p\sigma,b}\rangle$ the expression for both LCAO in terms of 2p atomic orbitals (see figure 1) is given by

$$|\chi^1_{p\sigma,b}\rangle = (1/\sqrt{2})[-|p_z(5)\rangle + |p_z(6)\rangle] \tag{5}$$
$$|\chi^2_{p\sigma,b}\rangle = (1/2)[|p_x(1)\rangle + |p_y(2)\rangle - |p_x(3)\rangle - |p_y(4)\rangle].$$

If $\alpha = a$, no LCAO corresponding to $|\chi^1_{p\sigma,a}\rangle$ and $|\chi^1_{s,a}\rangle$ exist and so only bonding with equatorial ligand orbitals is achieved.

As regards the metal wavefunction $|\varphi_{M,\alpha}\rangle$, it is given by

$$|\varphi_{M,a}\rangle = |x^2 - y^2\rangle$$
$$|\varphi_{M,b}\rangle = \mu_d|3z^2 - r^2\rangle + \mu_s|4s\rangle \qquad (\mu_d^2 + \mu_s^2 = 1) \tag{6}$$

pointing out the existence of 3d–4s hybridisation in the unpaired electron wavefunction,

but *only* for the compressed situation. For this case the unpaired spin densities on axial and equatorial ligand orbitals, $f_\sigma(AX), f_s(AX)$ and $f_\sigma(EQ), f_s(AX)$ are easily derived from (4) and (5) to be

$$f_\sigma(AX) = (N_b \lambda^1_{\sigma,b})^2/2$$
$$f_s(AX) = (N_b \lambda^1_{s,b})^2/2$$
$$f_\sigma(EQ) = (N_b \lambda^2_{\sigma,b})^2/2 \qquad (7)$$
$$f_s(EQ) = (N_b \lambda^2_{s,b})^2/2.$$

Similar relations between $f_\sigma(EQ), f_s(EQ)$ and the molecular orbital coefficients defined in (4) are obtained for an elongated situation.

For the present cases the theoretical expression for the SHF components, A^i_σ and A^i_s, are reasonably given by [22, 23]

$$A^i_\sigma = A^i_p + A^i_d$$
$$A^i_p = f^i_\sigma A^0_p$$
$$A^i_d = 2g_N \beta \beta_N / R^3_i \qquad (8)$$
$$A^i_s = f^i_s A^0_s$$

where as before i = 1 and i = 2 correspond to axial and equatorial ligands, respectively. The quantities $A^0_p = 463.4 \times 10^{-4}$ cm^{-1}, $A^0_s = 15\,192.9 \times 10^{-4}$ cm^{-1}, correspond to free F$^-$. The value $A^0_p = 463.4 \times 10^{-4}$ cm^{-1} has been calculated assuming $\langle r^{-3} \rangle_{2p} = 6.92$ au, instead of the pure Hartree–Fock value which is lower by 1.08, following the experimental results by Harvey [24] on atomic fluorine.

The expressions (8) neglect the admixture of the ground-state wavefunction with crystal-field and charge-transfer excited states via spin–orbit coupling. However, the inclusion of such an admixture (which is responsible for the g-shifts) in equation (8) only changes the A_σ values by less than 20% due to the high ionicity of the NiF$_6^{5-}$ complex [5, 22, 23].

The results of our calculations are collected in tables 1 and 2. First it is worth noting that for $N = 81$ the electronic charge of levels corresponding mainly to the NiF$_6^{5-}$ unit lies only less than 0.5% outside such a unit. This indicates that $|\varphi_R\rangle$ in equation (4) indeed plays a very minor role and thus the NiF$_6^{5-}$ unit is a good starting point for understanding the properties due to Ni$^+$ in fluorides.

As was already found by Messmer and Watkins in their SCCEH calculations on nitrogen-doped diamond [25] the calculated properties show a slight oscillatory dependence on the cluster size. Tables 1 and 2 point out that the results reached through both methods (SCCEH and MS X$_\alpha$) are rather comparable. This way both methods indicate that for the elongated NiF$_6^{5-}$ unit in LiF $f_s(EQ)$ (and $A_s(EQ)$) is much more sensitive than $f_\sigma(EQ)$ (and $A_\sigma(EQ)$) to variations of R_{EQ} (table 1). Also we have verified that the ratio between $\sqrt{f_s(EQ)}$ and the corresponding overlap integral $S_{s,a} = \langle x^2 - y^2 | \chi^2_{s,a} \rangle$ is practically independent of R_{EQ} in agreement with previous theoretical results [26, 27]. This kind of result supports the use of the experimental $A_s(EQ)$ for estimating R_{EQ} in the case of elongated NiF$_6^{5-}$ units as was firstly carried out in reference [28].

As regards the dependence on R_{AX} we have also verified that $f_\sigma(EQ)$ and $f_s(EQ)$ for the elongated case are practically independent of R_{AX} in the range 220 pm < R_{AX} < 260 pm (and for R_{EQ} = 210 pm) in agreement with the planar character of the b$_{1g}$ electron.

Table 1. Values of $f_\sigma(EQ)$, $f_s(EQ)$, $A_\sigma(EQ)$ and $A_s(EQ)$, corresponding to the *elongated* NiF_6^{5-} unit in LiF calculated via the SCCEH and MS X_α methods for several Ni^+–F^- distances R. Experimental values for the I centre in LiF are $A_\sigma = (12.5 \pm 1.5) \times 10^{-4}\,cm^{-1}$; $A_s = (51 \pm 2) \times 10^{-4}\,cm^{-1}$.

R_{EQ} (pm)	R_{AX} (pm)	Method and cluster size	$f_\sigma(EQ)$ (%)	$f_s(EQ)$ (%)	$A_\sigma(EQ)$ ($10^{-4}\,cm^{-1}$)	$A_s(EQ)$ ($10^{-4}\,cm^{-1}$)
200	243	SCCEH ($N = 7$)	1.23	0.77	8.80	116.98
		SCCEH ($N = 27$)	1.99	0.40	12.32	60.72
		SCCEH ($N = 81$)	1.43	0.40	9.72	60.77
		MS X_α ($N = 27$)	2.28	0.50	13.66	75.96
210	243	SCCEH ($N = 7$)	1.18	0.58	8.15	88.11
		SCCEH ($N = 27$)	1.98	0.32	11.86	48.61
		SCCEH ($N = 81$)	1.40	0.31	9.17	47.09
		MS X_α ($N = 27$)	2.25	0.37	13.10	56.21
213	243	SCCEH ($N = 7$)	1.16	0.53	7.94	80.52
		SCCEH ($N = 27$)	1.99	0.29	11.79	44.05
		SCCEH ($N = 81$)	1.40	.0.28	9.05	42.54
		MS X_α ($N = 27$)	2.24	0.34	12.95	51.66
213	233	SCCEH ($N = 7$)	1.16	0.53	7.94	80.52
		SCCEH ($N = 27$)	1.84	0.28	11.09	42.54
		SCCEH ($N = 81$)	1.30	0.27	8.59	41.02
		MS X_α ($N = 27$)	2.13	0.35	12.44	53.17

A main conclusion from table 1 is that for the elongated NiF_6^{5-} unit the theoretical values calculated around the previously estimated distance $R_{EQ} = 213$ pm [28] are not far from the experimental $A_\sigma \simeq 13 \times 10^{-4}\,cm^{-1}$ value found in Ni^+-doped fluoroperovskites [8–10] as well as in the I centre in LiF [1]. A similar agreement is encountered in the case of the isotropic SHF constant A_s.

As regards the compressed NiF_6^{5-} unit in LiF (table 2), both kinds of calculations performed for 200 pm $< R_{AX} < 230$ pm and $R_{EQ} = 237$ pm produce $f_\sigma(AX)$ values close to 2% and thus very similar to the values of $f_\sigma(EQ)$ reached for the elongated case. As a consequence of this all the calculated $A_\sigma(AX)$ values for the compressed NiF_6^{5-} unit in LiF are *at least three times smaller* than the experimental $A_\sigma(AX) \simeq 47.3 \times 10^{-4}\,cm^{-1}$ measured for the VII centre in LiF. Thus, the present facts strongly indicate that the assignment of the VII centre as pure Jahn–Teller, without any neighbour defect or impurity associated with Ni^+, is indeed rather dubious.

Other facts supporting this conclusion are:

(i) When an isolated d^9 impurity is placed in an 'initial' truly octahedral environment the stable situation has been found to be the elongated one. Good examples of this are found in the recent results on Ni^+-doped fluoroperovskites [8–10]. This assertion is supported theoretically by the expected positive sign of A_3 involved in the anharmonic term $A_3\rho^3 \cos(3\theta)$ [2] responsible for the distortion type. For $K_2ZnF_4:Cu^{2+}$ a *compressed* Cu^{2+} centre has been reported for which $g_\parallel$ is only equal to 2.003 [29]. However, the environment of Zn^{2+} which Cu^{2+} replaces is not perfectly octahedral, but axial ligands form slightly stronger Zn–F bonds than the equatorial ones. A similar situation seems to happen in $(ENH)_2 MnCl_4:Cu^{2+}$ [30, 31].

(ii) Values of $f_\sigma(AX) \simeq 10\%$ consistent with $A_\sigma(AX) = 47 \times 10^{-4}\,cm^{-1}$ are very difficult to reconcile with $f_\sigma(AX) = 6.7\%$ estimated [29] for the compressed CuF_6^{4-} centre

Table 2. Unpaired spin densities and $A_\sigma(\text{AX})$, $A_s(\text{AX})$ values, for the *compressed* NiF_6^{5-} unit in LiF calculated via the SCCEH and MS X_α methods, for several Ni^+–F^- distances R. Experimental values for the VII centre in LiF are $A_\sigma = (47.3 \pm 1.5) \times 10^{-4}\,\text{cm}^{-1}$ and $A_s = (102 \pm 2) \times 10^{-4}\,\text{cm}^{-1}$.

R_{EQ} (pm)	R_{AX} (pm)	Method and cluster size	$f_\sigma(\text{AX})$ (%)	$f_s(\text{AX})$ (%)	$f_\sigma(\text{EQ})$ (%)	$f_s(\text{EQ})$ (%)	$A_\sigma(\text{AX})$ ($10^{-4}\,\text{cm}^{-1}$)	$A_s(\text{AX})$ ($10^{-4}\,\text{cm}^{-1}$)
237	200	SCCEH ($N = 7$)	0.93	0.49	0.51	0.17	4.22	25.82
		SCCEH ($N = 27$)	1.47	0.27	0.97	0.10	6.35	15.49
		SCCEH ($N = 81$)	1.10	0.31	0.59	0.07	4.59	10.63
		MS X_α ($N = 27$)	1.85	0.19	1.33	0.22	8.02	33.42
237	207.5	SCCEH ($N = 7$)	1.10	0.49	0.48	0.15	4.08	22.78
		SCCEH ($N = 27$)	1.78	0.26	0.95	0.09	6.26	13.67
		SCCEH ($N = 81$)	1.31	0.30	0.57	0.07	4.50	10.63
		MS X_α ($N = 27$)	2.09	0.21	1.21	0.17	7.46	25.82
237	215	SCCEH ($N = 7$)	1.24	0.47	0.45	0.13	3.95	19.75
		SCCEH ($N = 27$)	2.09	0.26	0.91	0.08	6.07	12.15
		SCCEH ($N = 81$)	1.51	0.28	0.54	0.06	4.36	9.12
		MS X_α ($N = 27$)	2.34	0.23	1.08	0.13	6.86	19.75
237	230	SCCEH ($N = 7$)	1.41	0.39	0.38	0.10	3.62	15.19
		SCCEH ($N = 27$)	2.68	0.22	0.80	0.06	5.56	9.12
		SCCEH ($N = 81$)	1.78	0.21	0.48	0.05	4.08	7.60
		MS X_α ($N = 27$)	2.89	0.23	0.86	0.07	5.84	10.63
230	207.5	SCCEH ($N = 7$)	1.17	0.55	0.51	0.18	4.40	27.34
		SCCEH ($N = 27$)	1.83	0.29	0.85	0.10	5.97	15.19
		SCCEH ($N = 81$)	1.32	0.31	0.55	0.08	4.59	12.15
		MS X_α ($N = 27$)	2.17	0.26	1.07	0.19	7.00	28.86

found in $\text{K}_2\text{ZnF}_4 : \text{Cu}^{2+}$, because Cu^{2+} gives rise to more covalent bonds than the monovalent Ni^+ cation [5]. In this context it has been found from the analysis of NMR data that $f_\sigma(\text{EQ}) = 4.2\%$ for K_2CuF_4 is comparable to $f_\sigma(\text{AX})$ for $\text{K}_2\text{ZnF}_4 : \text{Cu}^{2+}$, but clearly higher than $f_\sigma(\text{EQ}) = 1.7\%$ derived for the elongated NiF_6^{5-} complex in LiF from EPR data [5, 23].

(iii) It was pointed out by Ham [7] that $\overline{\sin^2(\theta/2)}$ in equation (2) is likely to be higher than 0.97. Further arguments of this type have recently been reported by Riley *et al* [32].

Before concluding let us remark that again *both* methods indicate that for the compressed NiF_6^{5-} unit $f_\sigma(\text{AX})$ can increase when R_{AX} increases (table 2). This 'strange' behaviour opposite to that found in the elongated NiF_6^{5-} unit or in octahedral complexes like MnF_6^{4-}, CrF_6^{3-}, FeF_6^{3-}, etc [33, 34], appears because of the 3d–4s hybridisation in the antibonding a_{1g} level. In fact a decrease of $f_\sigma(\text{AX})$ upon increasing R_{AX} is obtained if the 4s orbital of Ni^+ is artificially suppressed from our basis.

A detailed insight into the origin of this surprising phenomenon will be reported in the near future.

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