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Ligand ENDOR of Cr³⁺ and Yb³⁺ ions in Cs₂NaInCl₆

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Abstract. The ligand and quadrupole interactions parameters have been measured at 4.2 K by ENDOR for three shells of ^{35,37}Cl, ¹³³Cs and ²³Na neighbours around Cr³⁺ and Yb³⁺ substitutional impurities. The ligand interaction parameters were analysed by means of expressions for spin densities obtained by the configurational interaction method. The quadrupole interaction parameters have been discussed in terms of a point-dipole model, the local deformation around the magnetic ions being taken into account.

Recently we have carried out an ENDOR investigation of the ligand interaction (LI) and quadrupole interaction (QI) of Cr³⁺ and Yb³⁺ ions in Cs₂NaYCl₆ elpasolite cubic crystal (Akhmin *et al* 1987a, b; Meiklyar *et al* 1987). The Cs₂NaInCl₆ crystal considered in this paper has the O_h⁵ space group down to liquid-helium temperature. The isomorphous substitution of In³⁺ by Cr³⁺ and Yb³⁺ provides the following coordination spheres of the paramagnetic centre: the nearest-neighbour regular octahedron of Cl⁻ ions, the next-nearest-neighbour regular cube of Cs⁺ ions and the next-next-nearest-neighbour regular octahedron of Na⁺ ions.

Cs₂NaInCl₆ single crystals doped with Cr³⁺ (0.003%) and Yb³⁺ (0.003%) were grown by the Bridgman technique and oriented with an x-ray diffractometer. The measurements of the LI and QI were carried out on an X-band 100 kHz field modulation ENDOR spectrometer at $T = 4.2$ K.

The EPR spectra of Cr³⁺ (3d³, Γ_2) and Yb³⁺ (4f¹³, Γ_6) even isotopes were single lines with $g = 1.981(1)$ and $g = -2.584(1)$, respectively.

The ENDOR spectra of ^{35,37}Cl, ¹³³Cs and ²³Na nuclei were recorded in the 0.3–25.0 MHz frequency range. The peculiarities of the ENDOR spectrum recorded were similar to those observed for Cs₂NaYCl₆: Cr³⁺, Yb³⁺ (Akhmin *et al* 1987a, b); in particular no ENDOR responses of the Cl⁻ ions in Cs₂NaInCl₆: Yb³⁺ were detected for $M = \frac{1}{2}$, whereas for $M = -\frac{1}{2}$ all six possible transitions were observed.

The dependence of the ENDOR transition frequency on the magnetic field direction in the {001} crystal planes was analysed in order to identify ENDOR transitions by electron and nuclear states unambiguously. The angular dependence approximated by the theoretical curves was obtained by numerical diagonalisation of the matrix of the nuclear spin Hamiltonian:

$$\mathcal{H}_n = A_{\parallel} S_z I_z + A_{\perp} (S_x I_x + S_y I_y) + (P/3)[3I_z^2 - I(I+1)] - g_n \beta_n H I_z$$

where z is the direction of the metal–ligand bond.

The LI and QI parameters are given in table 1. The signs of Cl⁻, Cs⁺, Na⁺ \leftrightarrow Cr³⁺ LI parameters are absolute and were determined on the basis of the following facts.

Table 1. LI and QI parameters for M-Cl⁻, Cs⁺, Na⁺ in Cs₂NaInCl₆; M (M ≡ Cr³⁺, Yb³⁺). Here $A_d = g_n \beta_n \beta_n / R^3$. The experimental error is ±0.003 MHz.

Ion	Nucleus	A_{\parallel} (MHz)	A_{\perp} (MHz)	A_s (MHz)	A_p (MHz)	A_d (MHz)	P (MHz)
Cr ³⁺	³⁵ Cl	-7.191	+0.420	-2.117	-2.537	+0.421	6.037
Cr ³⁺	³⁷ Cl	-5.985	+0.350	-1.761	-2.112	+0.350	4.752
Cr ³⁺	¹³³ Cs	+1.402	+0.904	+1.070	+0.166	+0.109	0
Cr ³⁺	²³ Na	-0.140	-0.459	-0.353	+0.106	+0.141	0.142
Yb ³⁺	³⁵ Cl	+1.908	+2.778	+2.488	-0.290	-0.543	2.069
Yb ³⁺	³⁷ Cl	+1.588	+2.312	+2.070	-0.241	-0.456	1.628
Yb ³⁺	¹³³ Cs	-0.256	+0.137	+0.005	-0.132	-0.141	0
Yb ³⁺	²³ Na	-0.244	+0.117	-0.003	-0.120	-0.185	0.122

(i) For ²³Na and ¹³³Cs nuclei the anisotropic part of the LI has similar values and the same sign as the dipole-dipole interaction A_d (table 1). It enabled us to identify the ENDOR transitions of these nuclei by electron quantum states and to determine the absolute signs of their LI parameters.

(ii) The intensity of ENDOR signals was considerably dependent on the attribution of ENDOR transitions to electron quantum states. The identification of ENDOR transitions by electron quantum states for ^{35,37}Cl nuclei was based on the presence of this dependence for all nuclei in the case of the known identification (i).

(iii) To determine the absolute signs of the ^{35,37}Cl LI parameters with respect to the absolute signs of the ²³Na and ¹³³Cs LI parameters, the field dependence of the frequencies of ENDOR transitions within the EPR linewidth of the Cr³⁺ ion has been investigated.

In the case of the Yb³⁺ ion we obtained the signs of parameters using the assumption of Akhmin *et al* (1987b). The signs are absolute as well. The signs of the QI parameters were not determined.

To estimate the parameters of covalency of the ligands in Cs₂NaMCl₆: Cr³⁺ (M ≡ Y, In) the expressions for spin densities obtained by Anikeenok and Eremin (1981) by the configurational interaction procedure up to the third order of the perturbation theory, when there is no metal-ligand σ bond, were used. When the effects of charge transfer in the 4s impurity orbitals are neglected, one has

$$f'_s = -6(2B + C)\{[(3s|3d_0) + \gamma_{3s,3d_0}]/\Delta_{3s,3d}\}\gamma_{3s,3d_0}$$

$$f'_\sigma = -6(2B + C)\{[(3p_0|3d_0) + \gamma_{3p_0,3d_0}]/\Delta_{3p,3d}\}\gamma_{3p_0,3d_0}$$

$$f_\pi = [(3p_1|3d_1) + \gamma_\pi]^2$$

where $B = 918 \text{ cm}^{-1}$ and $C = 4133 \text{ cm}^{-1}$ are Racah parameters for Cr³⁺ (Abragam and Bleaney 1972). To obtain order-of-magnitude estimates the following values of parameters are taken: the energy of electron transfer from the 3p shell of Cl⁻ to the 3d shell of Cr³⁺ is given by $\Delta_{3p,3d} \approx 40\,000 \text{ cm}^{-1}$ (Eremin 1982); since $\Delta_{3s,3p} \approx 130\,000 \text{ cm}^{-1}$ (Clementi and Roetti 1974), the transfer energy $\Delta_{3s,3d} \approx 170\,000 \text{ cm}^{-1}$. Overlap integrals were estimated using Hartree-Fock states of electrons of Cr³⁺ and Cl⁻ ions (Eremin *et al* 1977) and are given in table 2. The reduction in the elpasolite lattice constant at $T = 4 \text{ K}$ was taken into account. The values of covalency parameters given in table 2 were obtained for $f'_s = -0.1\%$, $f'_\sigma = -1.6\%$ and $f_\pi = 3.6\%$ in Cs₂NaYCl₆:Cr³⁺ and for $f'_s = -0.1\%$, $f'_\sigma = -2.0\%$ and $f_\pi = 3.1\%$ in Cs₂NaInCl₆:Cr³⁺.

Table 2. Numerical values of overlap integrals and estimates of covalency parameters. The lattice parameter at 4 K is $\alpha = 1.065$ nm for Cs_2NaYCl_6 and $\alpha = 1.045$ nm for $Cs_2NaInCl_6$.

	Cs_2NaYCl_6	$Cs_2NaInCl_6$	ABF_3
$(3p_1 3d_1)$	0.02217	0.02395	
$(3s 3d_0)$	0.02612	0.02837	
$(3p_0 3d_0)$	-0.04467	-0.04724	
$\gamma_{3s,3d_0}$	0.057(10)	0.060(10)	0.05 ^a
$\gamma_{3p_0,3d_0}$	0.157(10)	0.174(10)	0.13 ^a
γ_π	0.168(10)	0.151(10)	

^a Anikeenok and Eremin (1981).**Table 3.** Local deformation in QI parameters. The sign of displacement from the impurity ion is positive.

Crystal	ΔCl (pm)	P_{lat} (MHz)	P_{add} (MHz)	P_{total} (MHz)	P_{exp} (MHz)
$Cs_2NaYCl_6:Cr^{3+}$	-14.3(5)	+0.09(2)	+0.15	+0.24	0.286 ^a
$Cs_2NaInCl_6:Cr^{3+}$	-6.0(5)	+0.04(2)	+0.15	+0.19	0.142
$Cs_2NaYCl_6:Yb^{3+}$	-3.5(5)	+0.02(2)	-0.08	-0.06	0.038 ^b
$Cs_2NaInCl_6:Yb^{3+}$	+4.8(5)	-0.03(2)	-0.08	-0.11	0.122

^a Akhmin *et al* (1987a).^b Akhmin *et al* (1987b).

A small decrease in $\gamma_{3s,3d_0}$ and $\gamma_{3p_0,3d_0}$ should be expected when the electron transfer from 3s and 3p ligand shells to the 4s impurity orbitals is accounted for. It was shown by Anikeenok and Eremin (1981) that the contribution of this mechanism to f'_s and f'_σ is small and is about 10%. Thus, in the qualitative comparison of the covalency parameters in chlorine elpasolites with those in fluoride perovskites doped by transition-metal group ions, the covalent charge transfer to 4s shell of Cr^{3+} may be neglected.

Experimental or theoretical determination of the energy of charge transfer from 3s, 3p ligand shells to the 4f impurity shell is necessary for the calculation of LI parameters in $Cs_2NaMCl_6:Yb^{3+}$ ($M \equiv Y, In$), metal–ligand interaction mechanisms (Anikeenok *et al* 1982, 1984) being taken into account. Note that the estimates of the energy of electron transfer based on the ionisation energies and Madelung energies (Eremin 1978) resulted in a negative value of transfer energy in elpasolite, showing either the considerable effects of non-magnetic polarisation of ligands or the need to take into account other contributions of at least equal importance.

According to the results of previous papers on the LI in chlorides the interaction between the impurity ions and distant nuclei in $Cs_2NaInCl_6:Cr^{3+}, Yb^{3+}$ noticeably differs from the dipole–dipole interaction. Overlap and covalent charge transfer in the chain of adjacent ions $M-Cl^-Na^+$ ($M \equiv Cr^{3+}, Yb^{3+}$) also leads to a covalent contribution in the QI parameters of Cl^- and Na^+ ions.

As the position of Na^+ is cubic in elpasolite without an admixture, there is no electric field gradient (EFG) on its nucleus. The quadrupole splitting in the ENDOR spectra of ^{23}Na may be due to the EFG resulting from the local crystal deformation as the impurity paramagnetic ion is introduced into the lattice. The estimates of the QI parameters are given in table 3. Here ΔCl is the possible displacement of ligands according to the difference between the ionic radii of the impurity and the substituted ions; P_{lat} is a QI

parameter, calculated numerically within the charge-point model, the isotropic lattice relaxation and the decrease in lattice constant at $T = 4$ K being taken into account:

$$P_{\text{lat}} = \frac{3eQ(1 - \gamma_{\infty})}{4I(2I - 1)} \sum_i \frac{e_i(3 \cos^2 \vartheta_i - 1)}{(r_i + \Delta r_i)^3}$$

where $Q(^{23}\text{Na}) = 0.11$ b (Losche 1963), $\gamma_{\infty}(\text{Na}^+) = -4.6$ (Grechishkin 1973) are implied and Δr_i is a displacement of the ion from its position in the undistorted lattice. The displacements calculated using the power and exponential laws of lattice relaxation led to similar values of P_{lat} in our case. The values given in table 3 correspond to the power law $\Delta r_i = kr_i^{-\alpha}$, with $k = (\Delta\text{Cl})r_{\text{Cl}}^{\alpha}$ and $\alpha = 1$. The ionic radii for calculating ΔCl were taken from Weast (1970–1).

One can easily see that the explanation of experimental Q_1 parameters requires consideration of the additional contribution P_{add} . The values of P_{add} given in table 3 were estimated to make P_{total} and P_{exp} similar. The fact that P_{add} is the same for the same type of impurity ion is a consequence of the assumption of its covalent nature. Since the filled p orbitals of Na^+ produce no contribution to the EFG on its nuclei, it may be supposed that the mechanisms of the additional contribution are due to the decompensation of the filled shells and the formation of the effective positive hole in $2p_z$ orbitals of the Na^+ ion (Freund 1983).

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