

ENDOR STUDIES IN $[\text{Ir}(\text{CN}_4\text{Cl}_2)]^{4-}$ COMPLEX IN SODIUM CHLORIDE HOST LATTICE

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I. INTRODUCTION

The hyperfine interaction of the central metal unpaired electron on the $[\text{Ir}(\text{CN})_4\text{Cl}_2]^{4-}:\text{NaCl}$ complex with the host lattice sodium nearest neighbours were observed by ESR spectroscopy [1]. This complex is a low spin d^7 system of 2A_1 ground state with the unpaired electron occupying the metal d_{z^2} orbital. The large delocalization of the spin density on chlorine ligands and the shape of that orbital become possible the observation of the sodium atoms.

Recent ENDOR measurements on this system show the interaction of the unpaired electron beyond the ESR detectable sodium nearest neighbours of the complex, the spectra show the interaction with other sodium and chlorine groups of the host lattice shells.

II. RESULTS

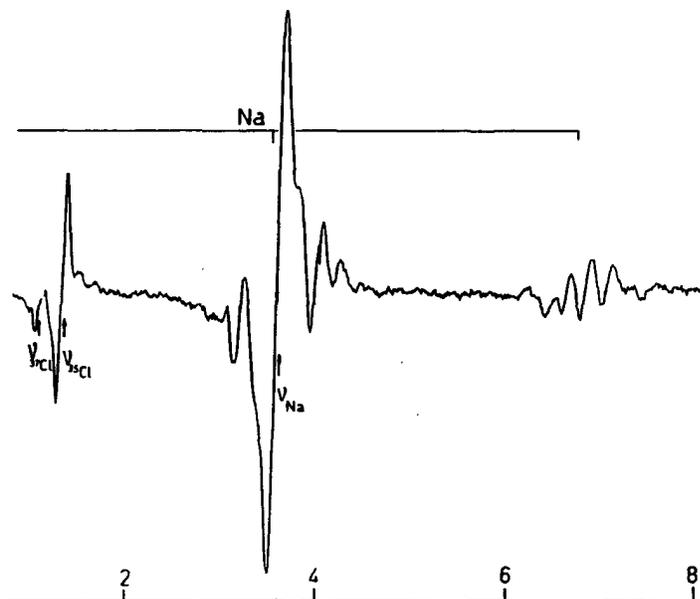
The ENDOR spectra, fig. 1, were obtained with a Bruker equipment at 15 K, using 5 mW microwave power, 70 W (50 Ω load) rf power and 0.25 MHz/s rate. ENDOR pattern of Na and Cl ($I=3/2$) consists of two groups of 2I lines each [2] separated by the hyperfine interaction A centered at ν_n , for $A/2 < \nu_n$, where ν_n is $g_n \beta_n B/h$, the magnetic resonance frequency of the nucleus in the fixed magnetic field at which the ENDOR spectrum is being observed. Within each group the lines are separated by the quadrupole interaction as the Electric Field Gradient due to all

ENDOR DATA (in MHz)

A_{\perp}^{Na}	$A_{\parallel}^{\text{Na}}$	A_{\perp}^{Cl}	$A_{\parallel}^{\text{Cl}}$
6.2	7.4 [†]	49.5 [†]	—
1.2	1.6	0.3	0.8
0.5	0.6	0.1	0.4
0.3	0.4		

[†] ESR detectable

FIGURE 1 - AT ESR PERPENDICULAR POSITION



surrounding ions depart from the cubic symmetry.

The spectra, fig. 2, also show the interaction of the unpaired electron with protons. These protons are incorporated into the lattice by growing the crystals in an aqueous environment.

The data corresponding to the interaction with the Na and Cl shells are presented in the table.

We conclude by this study that this paramagnetic species in alkali halide host lattices is really a large cluster involving immediated ligands of the central metal, lattice ions and even lattice impurities.

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REFERENCES

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- [2] L. Kevan and L. Kispert, Electron Spin Double Spectroscopy, John Wiley & Sons, 1976

FIGURE 2 - AT ESR PERPENDICULAR POSITION

