INVESTIGATION OF NUCLEAR HYPERFINE PROPERTIES OF NEODYMIUM CHLORIDE ($NdCl_3$) AS A RARE EARTH COMPOUND THROUGH CRYSTAL FIELD EFFECTS

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Abstract :- The present paper describes the nuclear hyperfine properties of $NdCl_3$with the help of crystal field theory. At first the crystal field parameters which are essential for the calculation of aforesaid properties are determined. The observed g-values of the sample were well explained with this theory with the comparison with some other samples. The nuclear hyperfine levels of ^{143}Nd for the sample has been determined . The hyperfine specific heat for$NdCl_3$ has shown an inverse T^2(where T represents temperature) rule in millikelvin temperature range .

Keywords : Crystal field effect, g-values, Hyperfine interaction, Hyperfine specific heat

1. Introduction :-

For rare earth family very few studies on Nd^{3+} compounds had been made as it is most abandoned unlike the other RE compounds. A Magnetic study on NdES [Ref 1] has shown that the ground term splitting is 308 cm^{-1} with |±5/2>as an eigenstate in ground state with anisotropy in g-values as $g_\perp < g_{II}$ .Then magnetic and EPR studies on different Nd^{3+} compounds furnish the same results [Ref 2,3]. Similar work has been done theoretically on $NdCl_3$ in 2015 [Ref 9]. Following that accordingly the nuclear hyperfine properties of the sample were determined.

2. Theoretical considerations :-

$NdCl_3$ has hexagonal structure having site symmetry C_{3h} for Nd^{3+} ion .Operating by the Hamiltonian obtained from crystal field effects given on $\left|J, m_J\right\rangle$ basis states of Nd^{3+} the CF energy levels and also the CF wavefunctions have been found out with the eigenstate |±5/2> as ground state and ground term splitting of nearly 303 cm^{-1}. Once the CF energy levels and corresponding wavefunctions are obtained, g values along symmetry axis and perpendicular to that were calculated which shows that $g_\perp < g_{II}$ by fitting the appropriate set of CF parameters B_2^0, B_4^0, B_6^0 and B_6^6 .

The Hyperfine Hamiltonian H_{hf} is given by

$$H_{hf} = [AS_zI_z + B(S_xI_x + S_yI_y)] + P\,[3I_z^2 - I(I+1)] \text{ where } P = \frac{e^2Q}{4I(2I-1)}\langle q_{zz}\rangle_T \quad \ldots\ldots\ldots \quad (1)$$

The term inside the first square bracket are due to nuclear magnetic hyperfine interaction, A and B are hyperfine constants, S is electronic spin and P is electric quadrupolar parameter. Generally in RE solids having a non-zero J value in the ground term, this term is more dominating. The crystalline electric field due to ligands produces an electric field gradient (EFG) at the nucleus. The second term of equation (2) is the product of EFG i.e $\langle q_{zz}\rangle_T$ and the nuclear quadrupole moment Q. EFG has two parts i.e lattice and 4f electronic part. $\langle q_{zz}\rangle_T = (1-\gamma_\infty)q_{zz}^{(latt)} + (1-R_Q)\langle q_{zz}\rangle_T^{4f}$ ……… .(2)

where γ_∞ and R_Q are lattice and atomic Sternheimer factors. For RE ion in static crystalline field the lattice contribution of EFG i.e q_{zz}^{latt} is considered to be temperature independent however the 4f electronic part of EFG i.e $\langle q_{zz}\rangle_T^{4f}$ is dependent on temperature. The thermal average of EFG is associated with CF energy values (E_ψ) and CF wave function(ψ)as

$$\langle q_{zz}\rangle_T^{4f} = \frac{\sum_{\psi=1}^{2J+1}\langle\psi|q_{zz}^{4f}|\psi\rangle\exp(-\frac{E_\psi}{k_BT})}{\sum_{\psi=1}^{2J+1}\exp(-\frac{E_\psi}{k_BT})} \quad \text{and} \quad \langle\psi|q_{zz}^{4f}|\psi\rangle = -\langle J\|\alpha\|J\rangle\langle r^{-3}\rangle_{4f}\langle\psi|3J_z^2 - J(J+1)|\psi\rangle$$

……… (3)

Here $\langle J \| \alpha \| J \rangle$ is operator equivalent to the hyperfine interaction. Similarly the lattice contribution of the EFG is related to the crystalline electric field as follows $q_{zz}^{(latt)} = -\frac{4B_2^0[(1-\gamma_\alpha)/(1-\sigma_2)]}{e^2\langle r^2\rangle_{4f}}$ …….(4)

Here B_2^0 is the CF parameter which was accurately obtained from theoretical calculation [8] and also other constants were calculated accordingly [Pelzl et al 1970] as Nd^{3+} ion is mirror image of Er^{3+} ion. Taking the average ionic radius and atomic no for ion the probable values of Q, $\langle r^2\rangle_{4f}$ and $\langle r^{-3}\rangle_{4f}$ were obtained.

3. Results and Discussion :-

3.1 The set of CF parameters, energy levels (both in cm^{-1}) and wavefunctions are given in Table-1 .

Table 1 - CF energy levels and CF wavefunctions of the sample

The most appropriate CF parameters are $B_2^0 = 52, B_4^0 = -61, B_6^0 = -44, B_6^6 = 625$

Crystal quantum No (μ)	Energy levels	Wavefunctions		Crystal quantu m No (μ)	Energy levels	Wavefunctions
5/2	-179.34	$0.901\left\|\pm\frac{7}{2}\right\rangle + 0.434\left\|\mp\frac{5}{2}\right\rangle$		(5/2)′	113.62	$0.434\left\|\pm\frac{7}{2}\right\rangle - 0.901\left\|\mp\frac{5}{2}\right\rangle$
1/2	-31.18	$\left\|\pm\frac{1}{2}\right\rangle$		(3/2)′	124.16	$0.658\left\|\pm\frac{9}{2}\right\rangle - 0.752\left\|\mp\frac{3}{2}\right\rangle$
3/2	-27.26	$0.752\left\|\pm\frac{9}{2}\right\rangle + 0.658\left\|\pm\frac{3}{2}\right\rangle$		*	*	*

Table 2 - g-values of different Nd-Compounds:-

Sample	Symmetry	g_{II}	$g_\perp$	Ref
$Nd^{3+}:LaCl_3$	C_{3h}	3.996	1.763	[1]
$Nd^{3+}:Y(OH)_3$	C_{3h}	3.630	1.960	[3]
NdES	C_{3h}	3.594	2.039	[4]
$NdCl_3$	C_{3h}	3.444	2.277	[9]

3.2 Nuclear Hyperfine properties :-

Operating H_{hf} on basis state $|I, m_I\rangle$, HF energy levels for ground(I_g=7/2) and first excited(I_e=9/2) state for ^{143}Ndwere determined.

It has been observed that the values of A/g_{II} and $B/g_\perp$ have almost constant values for RE compounds[Ref 7] . For this work value of A was taken as 200 MHz [Ref 8] and substituting g- values of the present work (Table-2), value of B were found and they are19.45×10^{-4} cm^{-1}and 44.0×10^{-4} cm^{-1} respectively. The nuclear ground term of ^{143}Nd (I_g=7/2) is followed by the first excited term (I_e=9/2) at few KeV above. The EFG for 4f-electronic part was calculated using the CF energy levels and wavefunctions (Table- 1) and its thermal variation is shown in Fig.1.The value of EFG becomes nearly constant below 25K. Taking the temperature-dependent and temperature-independent part of EFG , the value of electric quadrupole parameter for both ground (P_{gr}) and first excited state (P_{ex}) were computed. Both of them become temperature-independent at about 20 mK (Fig.2) . Using the values of A,B and P the hyperfine levels were calculated. Due to hyperfine interaction I_g(=7/2) with effective spin (S=1/2) splits into 7 doublets and 2 singlets with total width ~ 0.0249 cm^{-1} below 20 mK.. The first excited state I_e (=9/2) splits into 9 doublets and 2 singlets with total width~ 0.0316 cm^{-1} (Fig-3).

The HF specific heat was calculated using the following formula [Ref 6]

$$C_{hf} = \frac{Nk_B}{Z^2}[Z\sum_{i=1}^{m} X_i^2\exp(-X_i) - \{\sum_{i=1}^{m} X_i\exp(-X_i)\}^2]\text{where } X_i = \frac{E_i^{(0)}}{k_B T} \text{ and } Z = \text{partition function} \quad \text{……(5)}$$

here $E_i^{(0)}$ represents energy values of the HF split levels of nuclear ground state. Its value gives one peak at 11 mK with magnitude 0.6349R respectively (Fig. 4) and becomes nearly constant after 100 mK. It also varies as1/T^2(where T represents absolute temperature) over a large temperature range (between approximately 55mK and 5K , Fig. 5).

4. Conclusions

In crystal like $NdCl_3$ in which the CF parameters do not change with temperature it is possible to calculate some important hyperfine properties at millikelvin temperature range . Here the hyperfine constants A and B are found to be proportional to g_{II} and $g_{\perp}$ respectively and A is greater than B. Since q_{zz}^{latt} depends on only B_2^0 only the values of C_{hf} at different temperatures can be determined using corresponding formula (5). As C_{hf} obeys inverse T^2 law at millikelvin range i.e these values remain nearly constant of approximate value 236 mK^2 (Fig. 5) near to 100mK , this property may be useful for millikelvin thermometry.

Figures :-

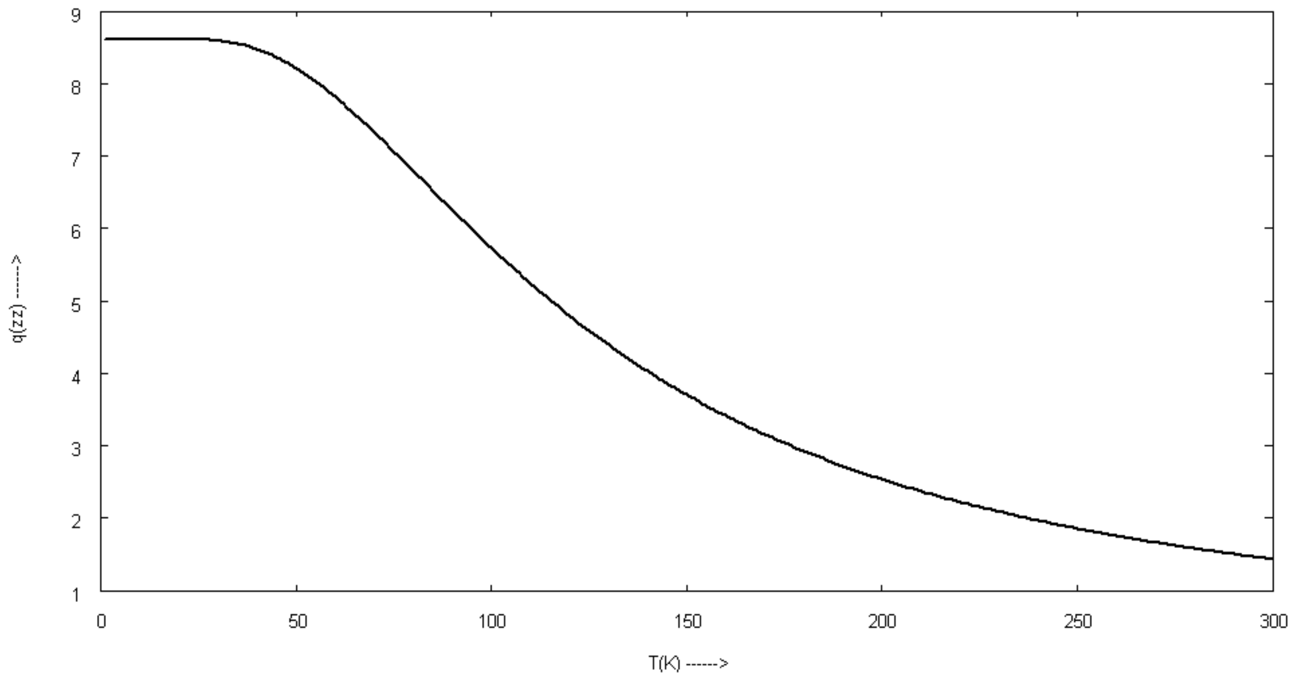

Fig.1 Thermal variation of 4f part of (EFG)

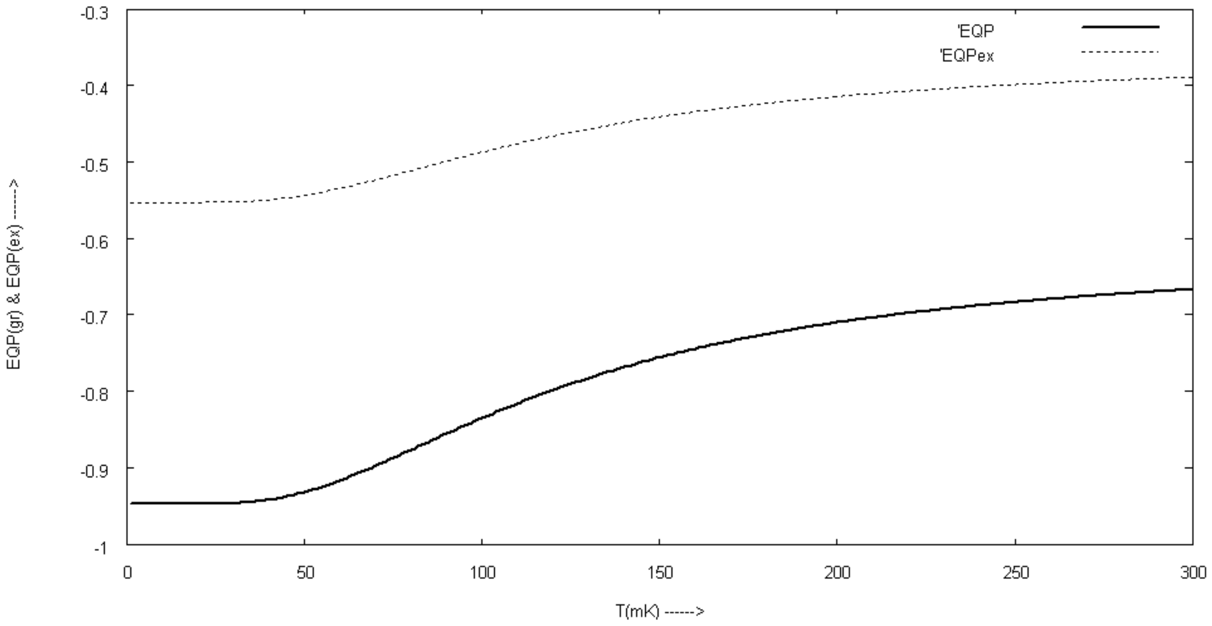

Fig.2 Thermal variation of P_{gr} (———) and P_{ex} (- - - -)

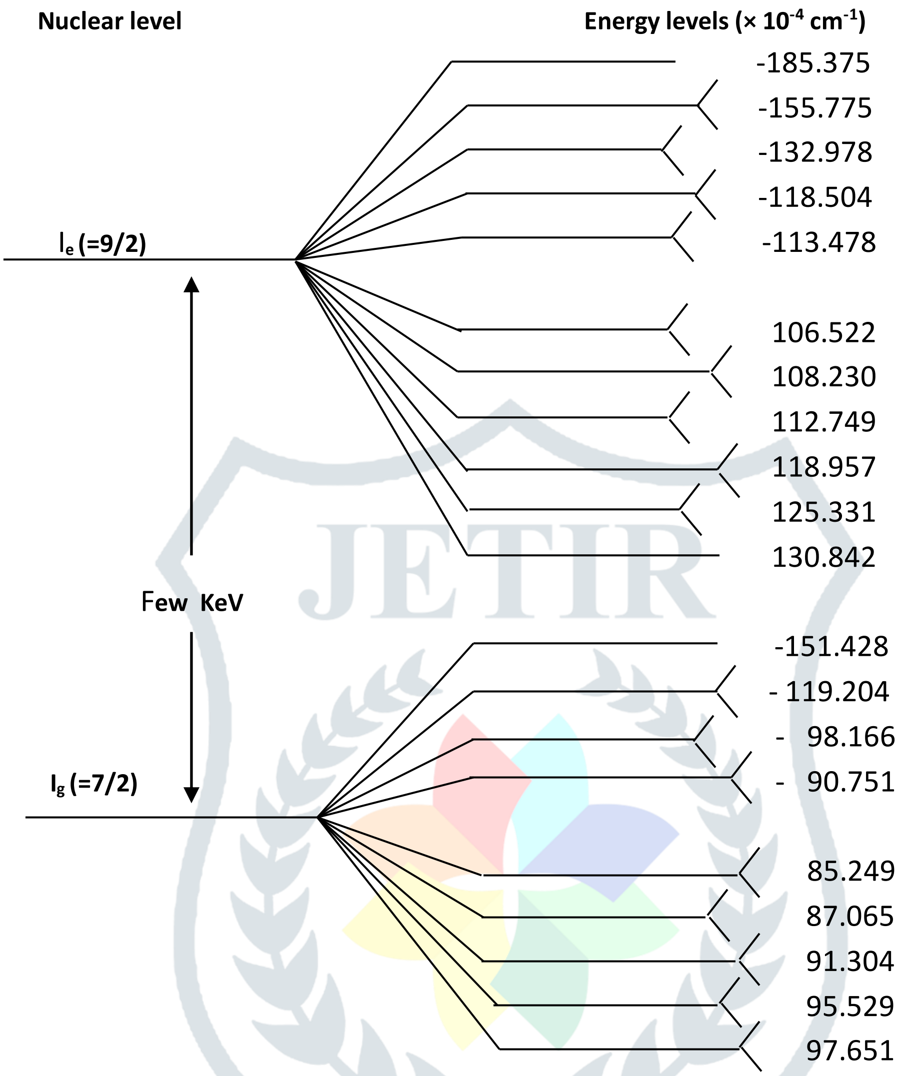

Fig.3 **HF energy levels for $^{143}NdCl_3$ (not in scale)**

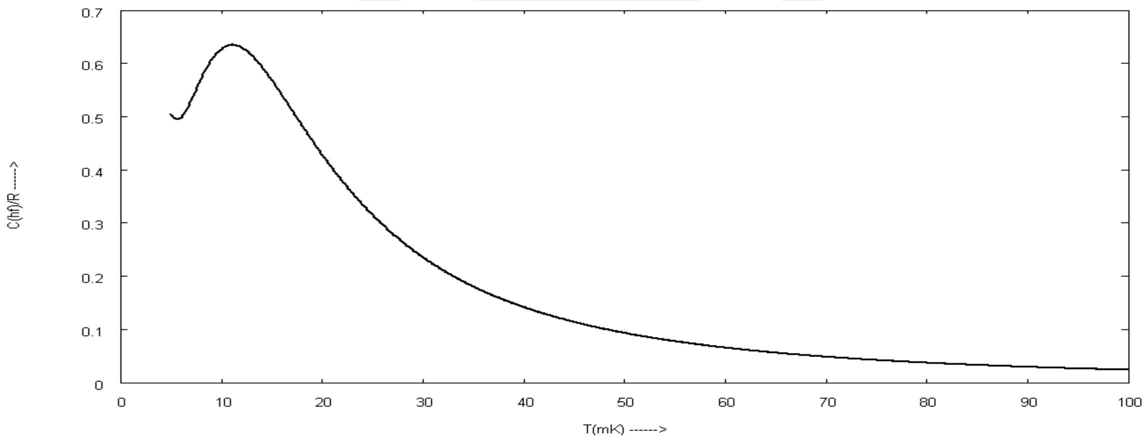

Fig .4 **Thermal variation of hyperfine specific heat**

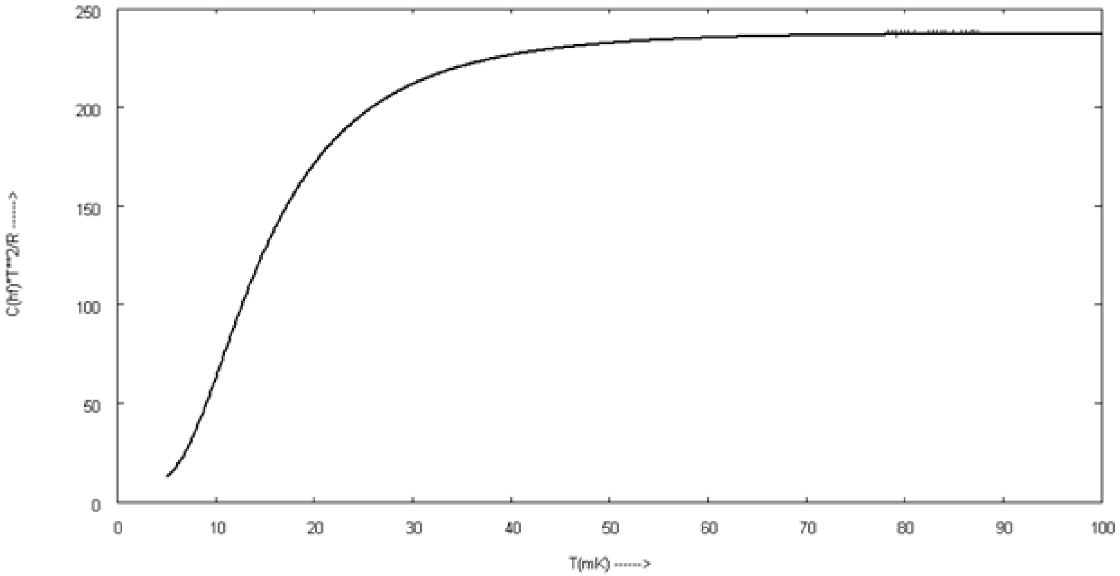

Fig. 5 Thermal variation of [C(hf)/R]×T^2 (in mK^2)

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