



# Thermal Variation of Different Components of Specific Heat for Neodymium Chloride (NdCl<sub>3</sub>) through Crystal Field Effects

<sup>1</sup>Somnath Bhattacharya and <sup>2</sup>Sulava Bhattacharyya

<sup>1</sup>Research Scholar, Department of Physics, Jadavpur University, Kolkata – 700032, India

<sup>2</sup>Research Guide, Department of Physics, Jadavpur University, Kolkata – 700032, India

**Abstract:** This paper reports the thermal variation of different specific heat components and entropy of NdCl<sub>3</sub>. The lattice component was calculated by adopting the empirical formula given by Chirico and Westrum (1980). The Schottky component was calculated between 10K and 300K using the crystal field energy levels. The hyperfine splitting of <sup>143</sup>Nd in NdCl<sub>3</sub> was found to be ~ 249×10<sup>-4</sup> cm<sup>-1</sup> and with these split energy levels the hyperfine specific heat was calculated. Only one peak of value 0.635R was observed at about 11mK.

**Keywords:** Crystal field effect, Schottky specific heat, Hyperfine interaction.

## 1. Introduction

In NdCl<sub>3</sub> crystal the site symmetry of Nd<sup>3+</sup> ion is C<sub>3h</sub> like ErCl<sub>3</sub>. Studies on magnetic, EPR optical properties of Erbium(III) compounds have been done extensively [ Dasgupta et al 1983 (10) , Dasgupta and Ghosh 1988 (9) , Chirico and Westrum 1980 (8)] since Er<sup>3+</sup> compounds are strongly magnetic and highly anisotropic . But similar studies on Nd<sup>3+</sup> compounds (which are mirror image of Er<sup>3+</sup>) are very few though it has only three 4f electrons. The magnetic moment of the specific ion is 3.62 BM and magnetic measurements on NdES have shown that ground term splitting is 308 cm<sup>-1</sup> with μ=±(5/2) as the ground state [Nath and Ghosh 1982 (1), Neogy et al 1984 (4)]. Magnetic and EPR studies on different Nd<sup>3+</sup> compounds [Abraham et al 1983 (7) and Dasgupta et al 1986 (9)] furnish that g- values along the symmetry axis is greater than that along perpendicular axis. Such aforesaid studies have not been done on NdCl<sub>3</sub> which has comparatively simple structure with high site symmetry of Nd<sup>3+</sup> ion.

Since the present paper reports the thermal variation of different specific heat components down to 10K (except for hyperfine specific heat) , we consider only the ligand field produced nine Cl<sup>-</sup> ions surrounding the Nd<sup>3+</sup> ion for this study. The ground term of Nd<sup>3+</sup> ion is <sup>4</sup>I<sub>9/2</sub> followed by first excited state <sup>4</sup>I<sub>11/2</sub> with energy gap 1867 cm<sup>-1</sup>. So consideration of crystal field (CF) theory will be preferred for theoretical calculation to evaluate the CF parameters and CF energy levels keeping all the aforesaid information of different Nd<sup>3+</sup> compounds in mind , to match the experimentally obtained g-values . From these values of CF energy levels the thermal variation of Schottky specific heat was evaluated over a wide range of temperature.

The calculation of lattice specific heat was done using the empirical formula given by Chirico and Westrum[8] and with the corresponding values of lattice specific heat obtained for LaCl<sub>3</sub> and GdCl<sub>3</sub>. At millikelvin temperature region the thermal variation of nuclear hyperfine specific heat was also estimated and it shows the inverse T<sup>2</sup> law, where T represents absolute temperature, over a certain temperature range.

## 2. Theoretical considerations

The total specific heat C<sub>T</sub> of the NdCl<sub>3</sub> crystal can be expressed as

$$C_T = C_L + C_{sh} + C_M + C_{hf} \dots \dots \dots (1)$$

where C<sub>L</sub> is lattice specific heat, C<sub>sh</sub> is Schottky specific heat, C<sub>M</sub> is magnetic specific heat and C<sub>hf</sub> is nuclear hyperfine specific heat. The last two terms i.e C<sub>M</sub> and C<sub>hf</sub> are important below 1K. Chirico and Westrum [8] gave an empirical interpolation formula to find out the values of C<sub>L</sub> for both RE-hydroxides and RE-trichlorides as follows

$$C_L\{LnCl_3\} = (1-f)\{C_L\{LaCl_3\}\} + f\{C_L\{GdCl_3\}\} \dots \dots \dots (2) \text{ where the f-factor is related to the molar volume}$$

$$(V) \text{ of } LaCl_3, GdCl_3 \text{ and } LnCl_3 \text{ according to the following relation } f\{LnCl_3\} = \frac{V\{LnCl_3\} - V\{LaCl_3\}}{V\{GdCl_3\} - V\{LaCl_3\}} \dots \dots \dots (3)$$

Between 10K and 300K as CF effects play the most important role in the solid , C<sub>sh</sub> becomes interesting. Its thermal variation was calculated using CF energy levels with the formula [5] :



$$C_{sh} = \frac{Nk_B}{Z^2} [Z \sum_{i=1}^m X_i^2 \exp(-X_i) - \{\sum_{i=1}^m X_i \exp(-X_i)\}^2] \dots\dots\dots (4)$$

where  $X_i = E_i^{(0)}/k_B T$  and  $Z =$  partition function here  $E_i^{(0)}$  represents the CF energy levels .

For the sample the total entropy has been computed over a wide range of temperatures.

The  $^{143}\text{Nd}$  (having nuclear spin  $I_g=7/2$ ) and quadrupole moment  $Q$  interacting with electric field gradient (EFG) produced by CF effects of neighbouring chloride ions will cause the splitting of nuclear levels. The nuclear specific heat was calculated in millikelvin temperature range. The hyperfine Hamiltonian is given by

$$H_{hf} = [ A I_z S_z + B (I_x S_x + I_y S_y) ] + P [ 3 I_z^2 - I(I+1) ] \dots\dots\dots (5)$$

where  $P = \frac{e^2 Q}{4I(2I-1)} \langle q_{zz} \rangle_T$  ..... (6) 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 interaction parameter (EQP) . The crystalline electric field due to ligands produces an EFG at the nucleus. The second term of eq-5 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.

$$\langle q_{zz} \rangle_T = (1 - \gamma_\infty) q_{zz}^{(latt)} + (1 - R_Q) \langle q_{zz} \rangle_T^{4f} \dots\dots\dots (7) \text{ where } \gamma_\infty \text{ and } R_Q \text{ are}$$

lattice and atomic Sternheimer factors.. The thermal average of EFG is associated with CF energy values ( $E_\psi$ ) and CF

wavefunction ( $\psi$ ) as  $\langle q_{zz} \rangle_T^{4f} = \frac{\sum_{\psi=1}^{2J+1} \langle \psi | q_{zz}^{4f} | \psi \rangle \exp(-\frac{E_\psi}{k_B T})}{\sum_{\psi=1}^{2J+1} \exp(-\frac{E_\psi}{k_B T})}$  and

$$\langle \psi | q_{zz}^{4f} | \psi \rangle = -\langle J || \alpha || J \rangle \langle r^{-3} \rangle_{4f} \langle \psi | 3J_z^2 - J(J+1) | \psi \rangle \dots\dots\dots (8) \text{ Here } \langle J || \alpha || J \rangle \text{ is}$$

operator equivalent to the hyperfine interaction. Similarly the lattice contribution of the EFG is related to the crystalline electric field as follows

$$q_{zz}^{(latt)} = -\frac{4B_2^0 [(1 - \gamma_\infty)/(1 - \sigma_2)]}{e^2 \langle r^2 \rangle_{4f}}$$

..... (9)

Here  $B_2^0$  is the first CF parameter which was accurately obtained from magnetic studies. The other nuclear constant values were taken from corresponding References. Operating by  $H_{hf}$  on basis state  $|I, m_I\rangle$  the HF energy levels for ground state as well as for first excited state ( $I_g=9/2$ ) for  $^{143}\text{Nd}$  were determined. The thermal variation of  $C_{hf}$  was calculated using equation(4) with the aid of the hyperfine split energy levels.

### 3. Results and discussions

With the help of crystal field theory we have determined the crystal field energy levels and the corresponding wavefunctions of  $\text{NdCl}_3$  .These are given in Table 1.

**Table 1** CF parameters (in  $\text{cm}^{-1}$ ),  $B_2^0=52$ ,  $B_4^0=-61$ ,  $B_6^0=-44$ ,  $B_6^6=625$

#### CF energy levels and CF wavefunctions of the sample

$\mu$	Energy levels( $\text{cm}^{-1}$ )	Wavefunctions
$\pm \frac{5}{2}$	-179.337	$0.901 \left  \pm \frac{7}{2} \right\rangle + 0.662.434 \left  \mp \frac{5}{2} \right\rangle$
$\pm \frac{1}{2}$	-31.180	$\left  \pm \frac{1}{2} \right\rangle$
$\pm \frac{3}{2}$	-27.263	$0.752 \left  \pm \frac{9}{2} \right\rangle + 0.658 \left  \pm \frac{3}{2} \right\rangle$

$\pm \frac{5}{2}$	113.621	$0.434 \left  \pm \frac{7}{2} \right\rangle - 0.901 \left  \mp \frac{5}{2} \right\rangle$
$\pm \frac{3}{2}$	124.159	$0.658 \left  \pm \frac{9}{2} \right\rangle - 0.752 \left  \pm \frac{3}{2} \right\rangle$

The factor ‘f’ for different RE-chlorides have been calculated and are shown in Fig-1 with the number of different 4f-electrons. For NdCl<sub>3</sub> the value of f was found to be nearly 0.58 .

The values of lattice and Schottky specific heat and entropy (S) at different temperatures for this sample are given in the following table . The thermal variation of C<sub>L</sub> and C<sub>sh</sub> are shown in Fig 2(a) & 2(b) .

**Table-2 Thermal nature of lattice and Scottky specific heat and entropy**

T (K)	C <sub>L</sub> /R	C <sub>sh</sub> /R	S/R
20	1.034	0.0047	0.673
40	4.545	0.2629	2.161
60	8.155	0.7067	4.066
80	11.905	0.9612	6.019
100	14.791	1.0165	7.821
120	16.813	0.9600	9.405
140	18.413	0.8435	10.713
160	19.623	0.7233	11.893
180	20.573	0.6420	12.943
200	21.276	0.5607	13.847
220	22.824	0.5058	14.582
260	22.679	0.3960	15.845
300	23.291	0.2863	16.918

This sample shows only one peak (Fig-2b) for the C<sub>sh</sub> vs T curve at 99.4 K with values 1.0193R. It has been observed that the peak value of C<sub>sh</sub>/R for Nd<sup>3+</sup> and Er<sup>3+</sup> compounds are very close to 1.0 (Cone 1972 and Dasgupta et al 1986).

The nuclear spin of <sup>143</sup>Nd in ground state is I<sub>g</sub>=7/2 followed by first excited state I<sub>e</sub>=9/2. With the help of g-values the hyperfine constants (A and B) were found out to be 19.45×10<sup>-4</sup> cm<sup>-1</sup> and 44.5×10<sup>-4</sup> cm<sup>-1</sup> respectively. The value of EFG for 4f-electronic part was calculated using the CF energy levels and wavefunctions (Table-1) and was found to be nearly constant at and below 25mK. Using the temperature dependent and temperature independent part of EFG the value of EQP for ground (P<sub>g</sub>) and first excited state (P<sub>e</sub>) were computed.

Using the values of A, B and P the hyperfine levels were calculated. Due to hyperfine interaction I<sub>g</sub>(=7/2) with electronic spin (S=1/2) splits into 7 doublets and 2 singlets with total width ~ 0.0249 cm<sup>-1</sup> (Fig-3) . The first excited state I<sub>e</sub> (=9/2) splits into 9 doublets and 2 singlets with total width~ 0.0316 cm<sup>-1</sup> . The hyperfine specific heat was calculated in millikelvin temperature range.

For this sample one peak was observed at 11 mK with magnitude 0.6349R [Fig-4a]. It also varies as 1/T<sup>2</sup> (where T represents absolute temperature) over a large temperature range (between 100 mK and 5K) with almost constant value (C<sub>sh</sub>/R)×T<sup>2</sup>=237 mK<sup>2</sup>[Fig-4b]. Since the hyperfine specific heat value is comparatively high (0.6R) and measurable hence this property can be used in millikelvin thermometry. Measurements of specific heat of other RE-chlorides are welcome for comparison with these results.

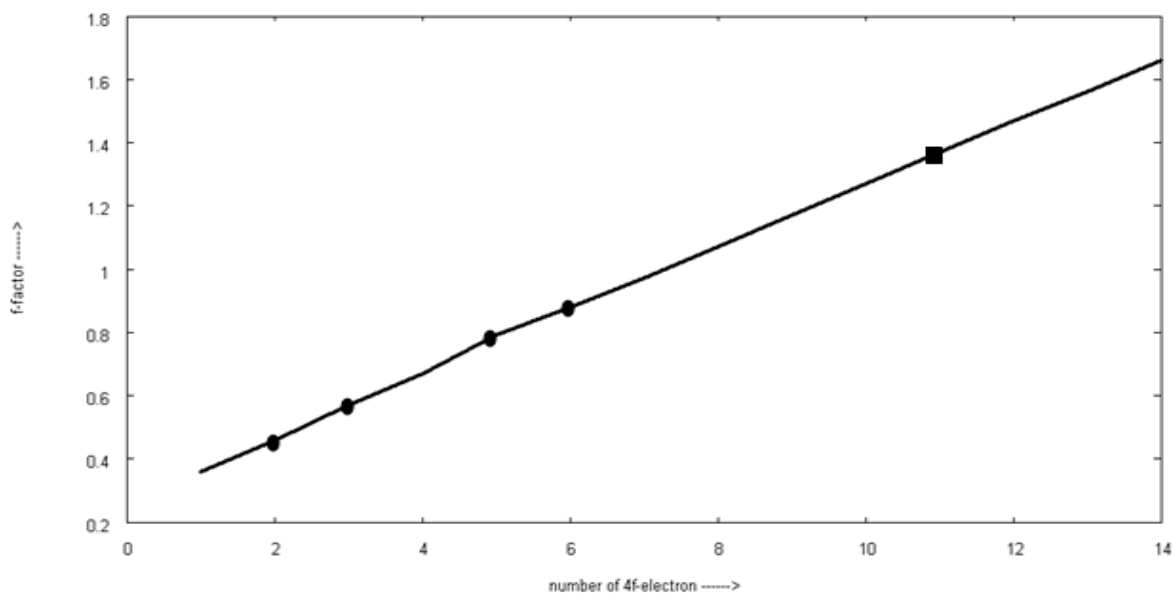


Fig -1 ( f-factor vs number of 4f-electron of RE ions )

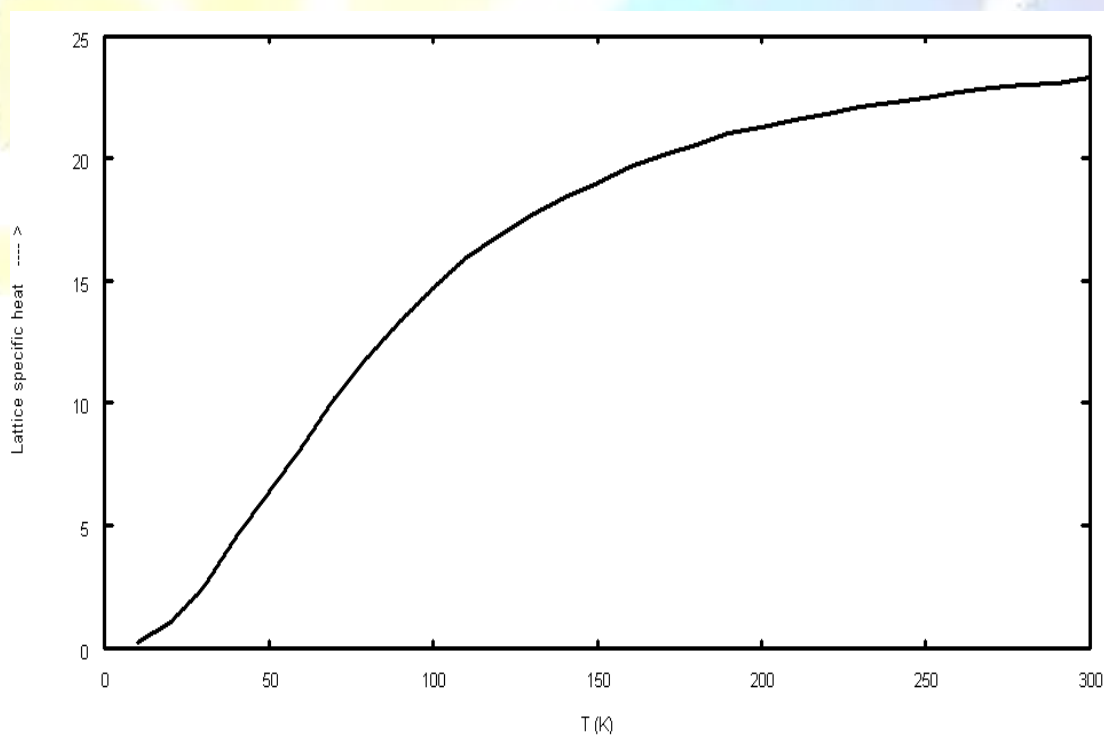


Fig2(a) Thermal variation of Lattice specific heat

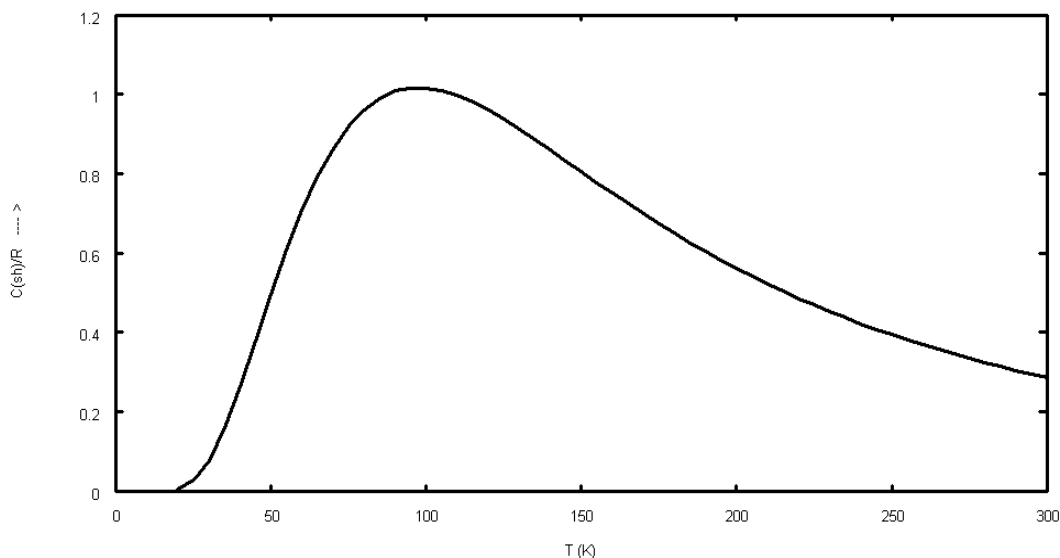


Fig2(b) Thermal variation of Schottky specific heat

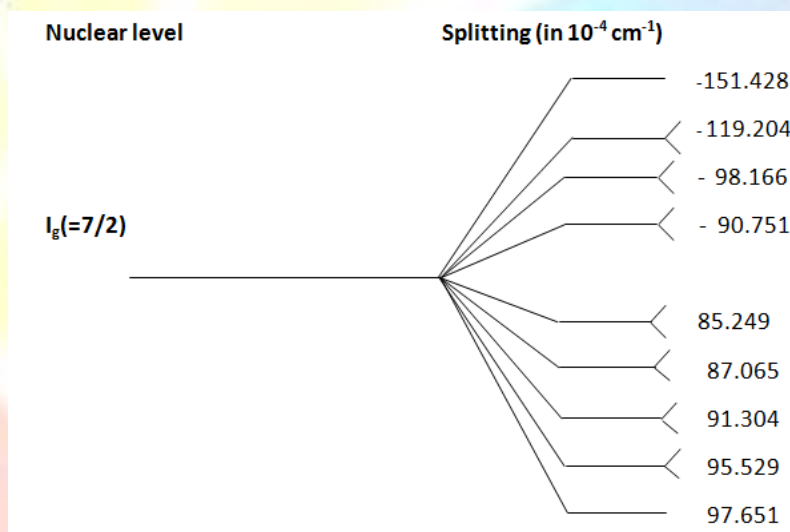


Fig 3 Hyperfine energy levels (not in scale)

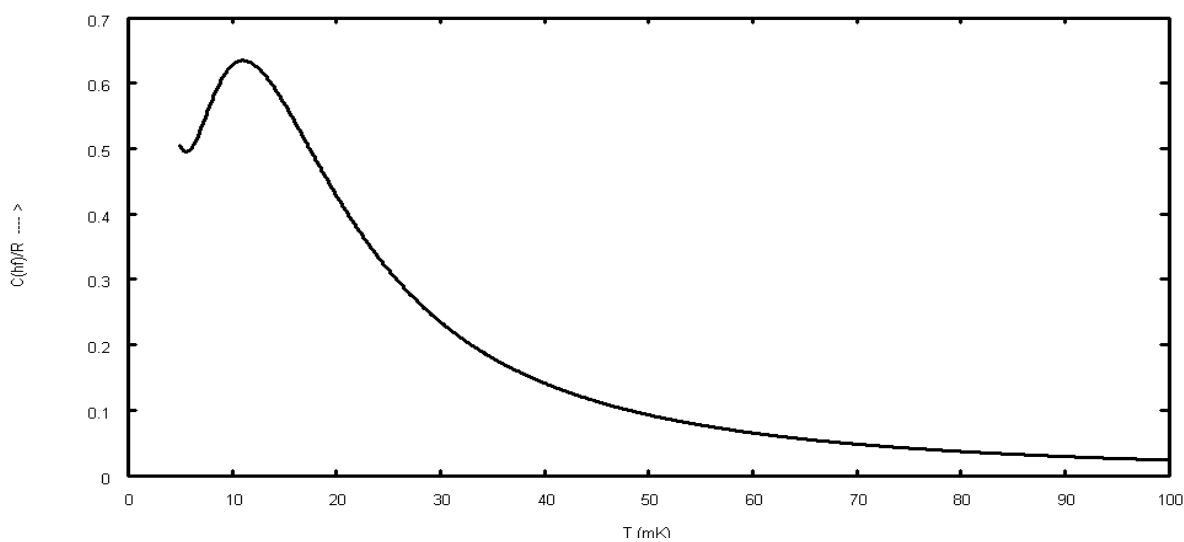
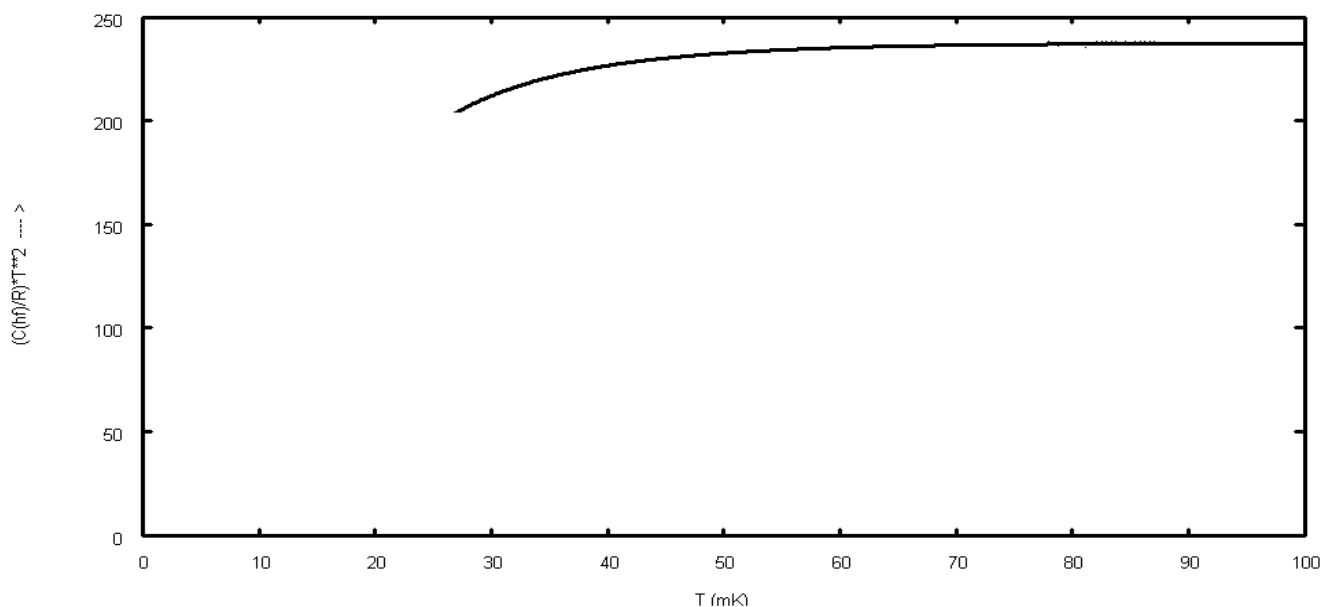


Fig-4a Thermal variation of Hyperfine specific heat



**Fig-4b Thermal variation of  $C_{hf}/R \times T^2$  ( in  $mK^2$ )**

## REFERENCES

- [1] A. Nath , U.S.Ghosh , Phys.Stat.Sol(b) 112, 187 (1982)
- [2] A.J.Freeman and R.E.Watson, Phys.Rev.132 , 706 (1963)
- [3] C.W.Fairall,J.A.Cowen and E.Grabowski, Phys.Lett.35A , 405 (1971)
- [4] D. Neogy, A. Chatterjee, T Purohit, J.Chem.Phys.80,3753 (1984)
- [5] J.A.Sommers and E.F. Westrum, J Chem. Thermodynamics, 9 , 1 (1977)
- [6] J.Pelzl , S Hufner and S.Scheller, Z.Phys, 231 , 377 (1970)
- [7] M.M.Abraham,L.A.Boatner,J.O.Ramey,M.Rappaz,J.Chem.Phys.78,3 (1983)
- [8] R.D.Chirico and E.F.Westrum (A-183), J-Chem.Thermodynamics,12, 717 (1980)
- [9] S.Dasgupta , M.Saha and D.Ghosh, J.Phys.Chem.Solids 45 , 589 (1984)
- [10] S.Dasgupta , M.Saha and D.Ghosh, J.Phys.C.Solid State Physics.19 , 1771 (1986)
- [11] S. Dasgupta and D. Ghosh, J.Appl.Phys.63(12), 5835 (1988)
- [12] S.Dasgupta,M.Saha,S.Mroczkowski and D.Ghosh, Phys.Rev.B.27,6960 (1983)