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Deuteration effect on the specific heat of nickel hexammine nitrate

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Abstract. In this paper the behaviour of the specific heat on NH_3 deuteration in nickel hexammine nitrate is determined from the analysis of different contributions of the crystal lattice. For a non-deuterated crystal the experimental specific heat outside the phase transition regions was reproduced well by the sum of harmonic oscillator specific-heat functions plus a correction for thermal dilatation. In calculating the specific heat, maximum use has been made of frequencies derived from spectroscopy. NH_3 deuteration provides a good test of the analysis procedure. Since deuteration generally shifts the frequencies of some of the vibrations, a hydrogenous compound and its deuterated analogue have different vibrational heat capacities. One would expect a larger heat capacity for a deuterated crystal; this is indeed observed by calorimetry. Hence, this model has to be verified by calculating and comparing with experiment how NH_3 deuteration affects the specific heat. The difference between the experimental NiDNO_3 and NiHNO_3 specific-heat values, referred to as $\Delta c_{\text{exp}}^{\text{D-H}}$, is expressed as the sum of the contributions from the frequency shifts in the vibrational spectrum of the deuterated crystal compared with that of the non-deuterated crystal. The results of the analysis show that the calculated $\Delta c^{\text{D-H}}$ is very close to the experimental values. This result strongly supports the simple Debye plus Einstein model.

1. Introduction

An interesting class of materials which exhibit phase transitions are hexammines described by the general formula $[\text{M}(\text{NH}_3)_6]\text{X}_2$ (MAX) where M denotes a divalent transition metal and $\text{X}^- = \text{Cl}, \text{Br}, \text{I}, \text{NO}_3, \text{ClO}_3, \text{ClO}_4, \text{BF}_4, \text{PF}_6$ or SO_3F . The best-studied compound of this class $[\text{Ni}(\text{NH}_3)_6](\text{NO}_3)_2$ (NiANO_3) undergoes structural phase transitions at $T_{c1} = 243$ K and $T_{c2} = 90$ K, and a glass transition at $T = 63$ K [10].

The specific heat has been measured for many hexammines including NiANO_3 [3–5] and its deuterated analogue $[\text{Ni}(\text{ND}_3)_6](\text{NO}_3)_2$ (NiDNO_3) [6]. NiDNO_3 undergoes phase transitions which have counterparts in NiANO_3 [6]. In this paper the specific heat outside the transition regions, i.e. the normal specific heat, will be considered. To derive the enthalpy and entropy of the phase transition, the experimental heat capacity is usually decomposed additively into the normal and transition parts. The estimation of the baseline is the usual procedure required to separate the anomalous part of the specific heat related to phase transitions from the remaining contribution from the crystal lattice. The baseline is usually determined by interpolation of the normal heat capacity into the transition region. The normal part consists of a vibrational contribution and a correction for thermal expansion.

An analysis of the smoothed experimental data, i.e. the normal specific-heat data, was undertaken. The detailed procedure of data analysis has been described in previous papers [1, 2]. Some of the aspects of the analysis will be briefly outlined and the effect of NH_3 deuteration will be considered and discussed.

A simple molecular model is commonly accepted in this type of crystal. The bonding within the complex ions has a covalent character and that between the complex cation and anion has an ionic character. This permits us to distinguish between external vibrations (lattice modes) and those related to the internal vibrations of the complex ions. The external modes are associated with the translational vibrations of the centres of mass of cations and anions as well as with torsional motions of the complex ions. Three types of molecular groups have been considered for hexammines:

- (1) $[\text{MN}_6]^{2+}$, octahedral skeleton of the complex cation with an octahedral symmetry, one group in a molecule;
- (2) (NH_3) , with a C_{3v} symmetry, one group at each of the octahedral vertices, and hence six groups in a molecule;
- (3) X^- , in the case of a nitrate, NO_3^- with a C_{3v} symmetry, two groups in a molecule.

It was assumed that each of the three acoustic modes could be represented by a Debye spectrum while all the other vibrations could be associated with the Einstein spectra. The Debye function with a characteristic temperature of 57 K, calculated for NiANO_3 [1], accounted for the contribution from acoustic modes. The other contributions from optical lattice modes including librations of the complex ions, internal vibrations of the complex ions, torsions, rocking modes and internal vibrations of NH_3 groups were found from the Einstein formula weighted by the corresponding mode degeneracy. The vibrational data provided by spectroscopy have been employed. The frequencies which could not be determined spectroscopically were taken from theoretical calculations or have been estimated [1]. The correction of c_V to c_P was also considered [2] since the Debye and Einstein models refer to conditions of constant volume.

According to this model, the differences $c_{\text{exp}}^{\text{D}} - c_{\text{exp}}^{\text{H}}$ can be assigned to the shifts of the frequency spectra and, supposedly, to the difference between the respective anharmonic contributions.

It was of particular interest to verify the model for nickel hexamine nitrate since the analysis of the specific heat of this crystal allows us to separate the contribution to the specific heat from NO_3^- oscillation in the high-temperature phase and to estimate the upper limit of the characteristic frequency of the oscillator [2].

2. Results and discussion

The effect of deuteration on the specific heat is to raise its experimental values. The heat capacity of NiDNO_3 measured experimentally [6] is indeed larger than that of NiANO_3 [3–5] in the whole temperature range studied, as expected. The upper curve in figure 1 traces the course of the heat capacity of NiDNO_3 from 100 to 260 K [6]. The lower curve in figure 1 represents the heat capacity of NiANO_3 [3–5]. The peaks in the specific heat related to the phase transitions at T_{c1} from the high-temperature cubic phase I to the cubic phase II are presented schematically while small anomalies related to the other phase transitions are omitted for clarity. We shall consider the difference $\Delta c_{\text{exp}}^{\text{D-H}}$ as given by

$$\Delta c_{\text{exp}}^{\text{D-H}} = c_{\text{exp}}^{\text{D}} - c_{\text{exp}}^{\text{H}}$$

i.e. the difference between the experimental heat capacities regarded as free from the anomalous contribution (i.e. the normal parts of the specific heat), for deuterated and non-deuterated crystals.

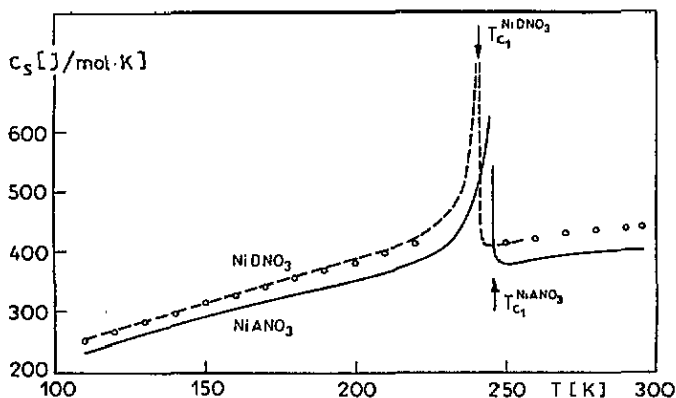


Figure 1. Experimental heat capacities of NiANO_3 [3-5] (—) and NiDNO_3 [6] (---) between 100 and 300 K; O, values calculated as $c_{\text{exp}}^{\text{NiANO}_3} + c_{\text{calc}}^{\text{D-H}}$.

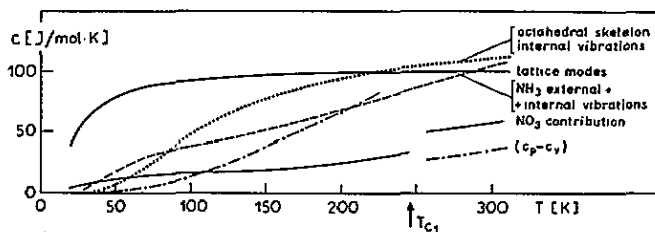


Figure 2. Calculated specific heat for NiANO_3 [1, 2] for all the contributions.

The normal specific heat consists of a vibrational contribution and a correction for thermal dilatation. The various harmonic contributions to the specific heat as well as the $c_p - c_V$ term [1, 2] for NiANO_3 are shown in figure 2. In the figure, four groups of vibrations can be distinguished. Two out of the five contributions presented in the figure exhibit a discontinuity at the phase transition ($T_{c1} = 243$ K). The first discontinuity, in $c_p - c_V$, results from the fact that this term was calculated from the thermodynamic equation

$$c_p - c_V = \beta^2 VT / X_T \quad (1)$$

where β , V and X_T represent the cubic expansion coefficient, molar volume and isothermal compressibility, respectively. This was done for phase I and phase II separately since all the data at $T = 292$ K (phase I) and at $T = 153$ K (phase II) were available. Next, the Nernst-Lindemann expression

$$c_p - c_V = A c_p^2 T \quad (2)$$

was used with A as an unknown parameter for phase I and phase II of NiANO_3 . Then, the same equation was used to account for the $c_p - c_V$ temperature dependence for phase I and phase II separately. Since the values of the coefficients A differ for the two phases, discontinuity appears. After summing all the contributions to the specific heat of NiANO_3 , excellent agreement has been obtained up to $T_{c1} = 243$ K, while above 243 K, the additional

contribution to the specific heat was clearly visible (figure 3) [2]. This was ascribed to the specific oscillation of NO_3^- groups in the high-temperature cubic phase I of NiANO_3 . This contribution, assumed for the high-temperature phase of the crystal and added to those due to the internal vibrations and NO_3^- torsions, shows a second discontinuity in figure 2. The assumed oscillation contribution is only a small part of the total heat capacity, and so any uncertainty in the other contributions drastically reduces the reliability of this assignment. We think the analysis of the NH_3 deuteration effect provides a test of this analysis.

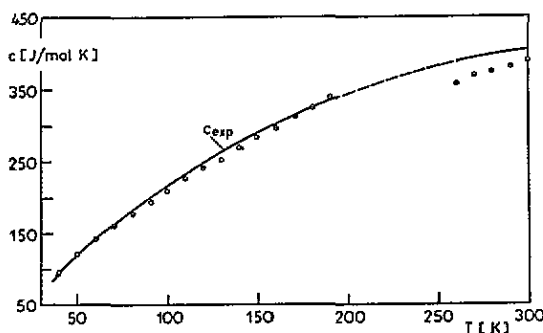


Figure 3. The experimental data on the specific heat for NiANO_3 , smoothed through the transitions (—): ---, phase transition at T_{c1} (anomalous region); O, values calculated as the sum of the following contributions: lattice modes, octahedral skeleton internal vibrations, NH_3 external plus internal vibrations, NO_3^- internal plus torsions, $c_p - c_v$. Above 250 K, an additional contribution is seen; this residual $c_{\text{exp}} - c_{\text{calc}}$ was ascribed to the oscillation of NO_3^- in phase I [2].

The possible effect of NH_3 deuteration on the contributions presented in figure 2 will be considered. Even if it is expected that the low-frequency external modes (lattice modes) will be shifted on deuteration as a natural consequence of the cation substitution [8], i.e. $[\text{Ni}(\text{NH}_3)_6]^{2+} \rightarrow [\text{Ni}(\text{ND}_3)_6]^{2+}$, they would actually have no effect on specific heat. These modes contribute with almost saturated values to the specific heat in this temperature range (above 100 K). The other vibrational contribution for NiDNO_3 , namely internal plus external NO_3^- modes including oscillation in the high-temperature phase, is assumed to be similar to that for NiANO_3 . The dilatation contribution to the specific heat of NiDNO_3 was also assumed to be the same as that of NiANO_3 because the unit-cell dimensions of the corresponding structures are similar for the two compounds [6, 11, 12].

The NH_3 contribution is significant and increases with increasing temperature in the temperature range considered (figure 2); so the effect of deuteration should be clearly seen and be possible to calculate if the required frequency data are available. Raman studies on deuterated hexammines have been published (CdDCl , CdDBr , CdDJ [7], NiDCl and NiDClO_4 [9]). The experiments showed that all the modes are shifted towards lower frequencies after deuteration. Since it was found that the frequencies either depend very little or do not depend on the anion and central metal atom type, and since in this model the specific heat is not very sensitive to the exact frequency value for a given number of degrees of freedom, we shall make use of these data in the following way. The Raman data available for deuterated and non-deuterated hexammines give the coefficients ν_D/ν_H , where ν_D is the frequency of a particular mode in the deuterated compound and ν_H that in the non-deuterated compound. These coefficients will account for the frequency shift of the modes for which the experimental data of the deuterated form are not available.

The ND_3 torsion modes are not Raman active. Probably because of the absence of translational symmetry for ND_3 groups in the crystal, the modes were observed in Raman spectra for CdCl_2 , CdBr_2 and CdI_2 [7]. The mean value of the frequencies assigned to ND_3 torsions in these hexammines was used to calculate the contribution from ND_3 torsions. One of the ND_3 rocking modes, $\rho(\text{T}_{2g})$, was also taken from the Raman study [7] and the shift of this mode on deuteration gave the coefficient ν_D/ν_H (equal to 0.74) for the other Raman-inactive rocking modes. The frequencies related to internal vibrations of NH_3 lie between 1100 and 3500 cm^{-1} . The stretching vibrations of NH_3 (above 3000 cm^{-1}) shift to the 2300–2600 cm^{-1} region after deuteration [9]. These high-frequency modes still lead to a negligible contribution to the specific heat. The other internal NH_3 vibrations shift from the 1100–1600 cm^{-1} to the 800–1200 cm^{-1} region [7, 9]. For these modes the coefficient ν_D/ν_H equals 0.73. Three out of all the ND_3 internal vibrations, i.e. $\delta(\text{A}_{1g})$, $\delta(\text{E}_g)$ and $\delta(\text{T}_{2g})$ (table 1), were taken as the mean value of the data for CdCl_2 , CdBr_2 and CdI_2 experimentally determined and reported in [7]. Finally, the internal vibrations of the octahedral skeleton $[\text{MN}_6]^{2+}$ were taken into account. The coefficients corresponding to frequency shifts on deuteration for this group of modes equals 0.93 [7, 9]. The frequency data are summarized in table 1. The wavenumbers in the table were obtained by multiplying the frequencies for non-deuterated crystals (from table 1 in [1]) by the appropriate coefficient ν_D/ν_H . With these assignments, the contribution to the specific heat for the deuterated crystal was calculated by means of independent Einstein functions including a factor of degeneracy:

$$c^D = \sum_j n_j N k_B \frac{(x_j^2 \exp(x_j))}{[\exp(x_j) - 1]^2} \quad (3)$$

where $x_j = \hbar\omega_j/k_B T$, n_j is the degeneracy of the j th mode, and the summation of Einstein functions is carried out over all the considered modes. Next, the contributions of the same modes for the non-deuterated crystal were subtracted from c^D .

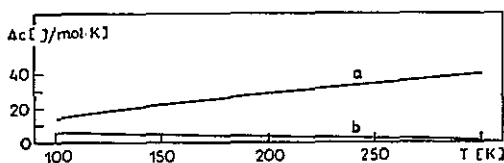


Figure 4. Two contributions to $\Delta c_{\text{calc}}^{D-H}$: line a, from NH_3 external (torsions and rocking modes) plus internal vibrations; line b, from internal vibrations of the octahedral skeleton.

The evaluated effects of deuteration on the NH_3 and octahedral skeleton vibrations are presented in figure 4. Δc is equal to the calculated c^D minus c^H for a given group of modes (i.e. the NH_3 internal plus external modes (torsions and rocking modes) and the internal vibrations of the octahedral skeleton). Hence, Δc represents the increase in the calculated specific heat due to the deuteration (i.e. beyond the value for the non-deuterated compound). The deuteration effect on the internal vibrations of octahedra is, as expected, small and decreases with increasing temperature. The increase in the specific heat after deuteration at higher temperatures is dominated by NH_3 torsions and rocking modes and by internal vibrations. The sum of these two contributions, presented in figure 4, gives $\Delta c_{\text{calc}}^{D-H}$.

This completes our analysis to account for the deuteration effect. The result is presented in figure 1 as open circles. The calculated points show excellent agreement with the

Table 1. Frequency data used in the calculation of the deuteration effect on the specific heat of NiDNO₃.

Mode of vibration	Symmetry of mode	Wavenumber (cm ⁻¹)	ν_D/ν_H	Reference
Internal vibrations of octahedra	A _{1g}	323	0.93	[7, 9]
	T _{1u}	307		
	T _{2u} {	275		
		244		
		218		
	E _g	207		
	T _{1u}	200		
T _{2g}	193			
Internal NH ₃	T _{1u}	803	0.73	[7, 9]
	A _{1g}	872	—	[7]
	E _g	839	—	[7]
	T _{2g}	1154	—	[7]
	T _{1u} } T _{1g} } T _{2u} }	1168	0.73	[7, 9]
NH ₃ torsions	A _{1g} + E _u + T _{1g}	97	—	[7]
NH ₃ rocking	T _{2g}	467	0.74	[7]
	T _{1u}	507		
	T _{2g}	467		
	T _{1u}	507		

and the calculated difference (shown as lines a and b in figure 4) between the hydrogenous and deuterated hexammine, i.e. $c_{\text{exp}}^{\text{NiANO}_3} + \Delta c_{\text{calc}}^{\text{D-H}}$. The way that the result is presented, i.e. $\Delta c_{\text{calc}}^{\text{D-H}}$ is added to the experimental data for the non-deuterated crystal, avoids cumulation of errors due to the rough approximation of the phonon spectrum of NiANO₃. The analysis has been made on the basis of data for this hexammine as well as for the related hexammine crystals.

In summary, the vibrational spectrum of a crystal was separated into the lattice and complex-ion modes. The specific heat was calculated [1, 2] by means of a combination of a Debye function (accounting for the acoustic modes) and an Einstein function weighted by the respective mode degeneracy. Maximum use has been made of the frequencies derived from spectroscopic studies. The $c_p - c_v$ correction was also determined. The analysis to account for the deuteration of NH₃ groups, within this model, has been applied in this paper. The effect of deuteration is to shift some of the characteristic frequencies. The increase in the specific heat due to the frequency shift after deuteration was calculated and compared with experiment. The agreement between the experimental specific heat of the deuterated crystal and that calculated within this model confirms the validity of the analysis. This result shows that all degrees of freedom as well as the $c_p - c_v$ correction have been satisfactorily accounted for.

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