

Order-disorder transition in ammonium copper chloride dihydrate*

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Abstract. The nature of the NH_4 network in the order-disorder transition of ammonium copper chloride dehydrate is examined.

Ammonium copper chloride dihydrate exhibits a broad specific heat anomaly between 120 K-200 K, which is attributed to order-disorder transition of ammonium ions (Suga *et al* 1965). A detailed laser Raman study of this transition has been undertaken at Trombay (Bansal *et al* 1979) with the object of (i) establishing the space group change in going through the transition and (ii) deducing the temperature variation of the order parameter.

The interest in this compound which belongs to tetragonal system arises due to the nature of its NH_4 network. Along z axis the adjacent NH_4 ions are at almost the same distance as in pure NH_4Cl , but in the x - y plane intervening copper water clusters enhance the separation by $\sim 4\%$. Thus from the point of NH_4 ordering, which is dominantly due to octupolar interactions ($\sim r^{-7}$) amongst the NH_4 ions, the system behaves as quasi-one-dimensional system, and this fact motivated our study.

The room temperature (300 K) space group for this crystal is designated by Wykoff to be D_{4h}^{14} , but for the fully ordered state ($\lesssim 100$ K) no information exists. From a polarised laser Raman study (using a 50 mW He-Cd laser and a grating double monochromator, both made in our laboratory), at 300 K and 100 K (see table 1), it has been deduced (Bansal *et al* 1979) that while room-temperature-space-group assignment of D_{4h}^{14} is correct, new modes appear at 100 K, implying a lowering of crystal symmetry. In fact it has been shown (Bansal *et al* 1979) that the low temperature space group is D_{2d}^3 .

Finally, to arrive at the temperature variation of the order parameter, m (defined as the difference between the fractional number of NH_4 ions in the two possible orientations) a temperature-dependent study of the Raman intensity of some modes has been made. Since the Raman intensity I for some modes lying between 140 cm^{-1} - 220 cm^{-1} is approximately related to m via the relation

$$I \sim |A + mB|^2, \quad A, B \text{ being constants,}$$

*Work done in collaboration with Drs A P Roy and M L Bansal.

Table 1. Spectra of $(\text{NH}_4)_2\text{CuCl}_4 \cdot 2\text{H}_2\text{O}$. All frequencies are in cm^{-1} .

Polarizability Component	Raman active modes for D_{4h}		Modes observed at 100 K		Maximum no. of new modes expected for subgroups of D_{4h}						
	Allowed*	Observed (300 K)	Common with 300 K	New modes	C_{4h}	D_{2h}	D_4	C_{4v}	D_{2d}^{**}	D_{2d}^{**}	
ZZ	Nw 0	1	0	1	0	1	0	
	Na 1	320	320	..	1	0	0	0	1	1	
	Nr 3	118	127	78	152	2	0	1	4	0	4
		223	225	410							
XX-YY or XY	Nw 1	532	546	626	0	0	0	0	0	1	
	Na 0	0	0	1	1	0	0	
	Nr 3	92	96	160	117	0	0	4	4	4	1
		198	204								
XY	Nw 0	0	1	0	1	1	0	
	Na 1	0	1	0	1	0	0	
	Nr 4	131	138	136	153	0	2	0	0	1	4
		183	190								
	244	247	390	402							
ZX	Nw 2	683	684	610	0	0	0	2	2	2	
	Na 2	302	302	..	0	0	0	2	2	2	
		346	346
	Nr 6	72	70	60	0	0	0	9	9	9	
		100	107	77 (?)
		122	128	100
		155	170	196
172	188		
242	248		

* Nw and Na designate librations of H_2O and NH_4 respectively and Nr others.

** Vertical mirrors of D_{2d}^{**} contain X, Y axes, those of D_{2d} are equi-inclined to X, Y axes.

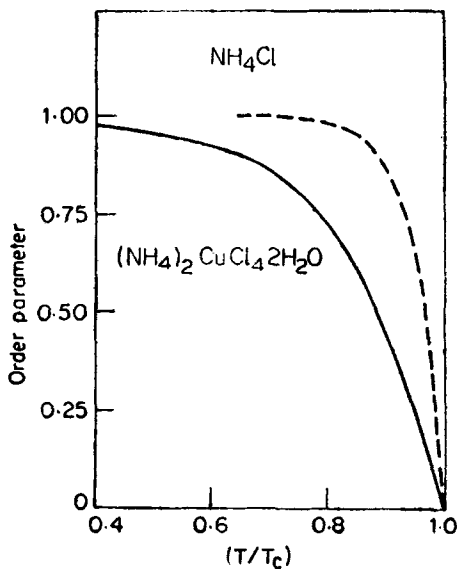


Figure 1. Comparison of the temperature variation of order parameter for the three-dimensional system NH_4Cl with that measured for the quasi-one-dimensional system $(\text{NH}_4)_2\text{CuCl}_4 \cdot 2\text{H}_2\text{O}$.

it is possible to deduce the temperature variation of m itself from the measured values of I . The measured temperature variation of m shows a much more gradual change (Roy *et al*) as compared to the results for pure NH_4Cl (figure 1).

References

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Suga H, Sorai M, Yamanaka T and Seki S 1965 *Bull. Chem. Soc. Jpn.* **38** 1007