

Crystallographic and magnetic phase transition in TlMnCl_3

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Abstract. The results of our NMR, EPR and magnetic susceptibility measurements in the paramagnetic state of TlMnCl_3 are reported here. The NMR paramagnetic shift of thallium is found to be small but positive. Mn^{2+} EPR line is exchange narrowed. The susceptibility measurements indicate an antiferromagnetic transition. The heat of crystallographic phase transition ΔH , in TlMnCl_3 has been measured using differential scanning calorimetry. The crystallographic phase transition appears to be first order and ΔH is unusually low viz. 10 cal mole⁻¹. In the case of KMnF_3 ΔH , which is reported here for the first time, is determined to be 2 cal mole⁻¹.

Keywords. Phase transition, antiferromagnetic; differential scanning calorimetry; TlMnCl_3 ; KMnF_3

1. Introduction

Many ionic compounds of the ABX_3 type crystallise in the perovskite structure in which B ions are situated in the holes created by close packing of AX_3 layers. TlMnCl_3 belongs to this class of compounds. In a recent paper, Melamud *et al* (1971) have discussed in detail the similarities in many physical features of TlMnCl_3 and KMnF_3 , another member of the ABX_3 perovskite family. Both undergo a cubic \rightarrow tetragonal crystallographic phase transition, believed to be due to the softening of the Γ_{25} phonon mode. The magnetic ions (Mn^{2+}) in both these compounds are known to order into an antiferromagnetic arrangement (of G-type) below their respective Neel temperatures. Further, the Goldshmidt number for both of these is the same (~ 0.88) whereas the commonly encountered number in perovskites is in the range of 0.90–0.93. KMnF_3 has been studied extensively by many different physical techniques such as neutron diffraction (Minkiewicz and Shirane 1969), x-ray diffraction (Minkiewicz *et al* 1970), EPR (Gulley *et al* 1969), NMR (Shulman and Stuart 1961, Minkiewicz and Nakamura 1966) (of F^{19} and Mn^{55}), etc. On the other hand, no results of the NMR, EPR, susceptibility and heat of transition measurements are available for TlMnCl_3 . In this paper, we present the results of our measurements on TlMnCl_3 and KMnF_3 .

2. Preparation

The sample of polycrystalline TlMnCl_3 was made by heating equimolar quantities of TlCl and $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ in a stream of dry Cl_2 gas instead of HCl (Kestigian 1970). An

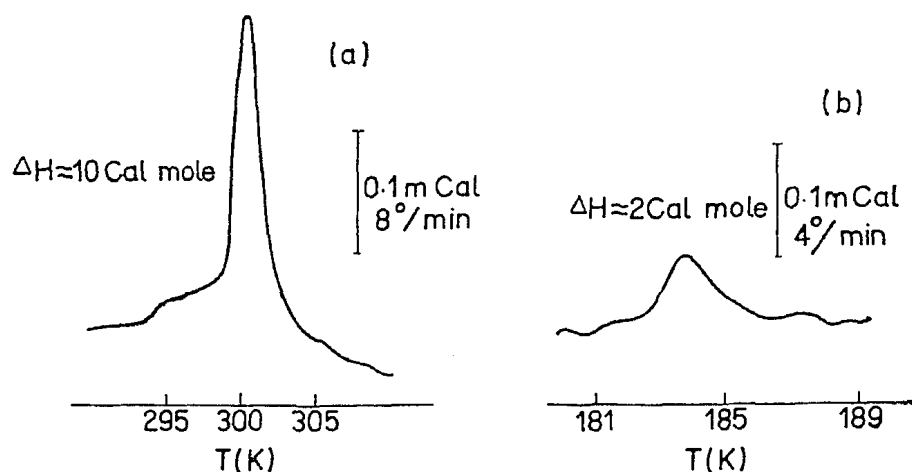


Figure 1. DSC Scans of (a) TiMnCl_3 (132 mg) and (b) KMnF_3 (80 mg)

orange coloured lump was obtained. TiMnCl_3 was always handled in a drybox under dry nitrogen. The cell-constants of a single crystal grown from this powder of TiMnCl_3 agreed very well with those reported in literature. Chips of single crystal KMnF_3 were made available to us by Dr S Mitra. Finely ground powder of a few of these chips was used. A Perkin-Elmer DSC 1B was used for differential scanning calorimetric (DSC) work. For magnetic susceptibility the standard Gouy technique was used. A Varian Associates wide line NMR Spectrometer was used for all NMR measurements. Thallium NMR was observed at 7, 9, 12 and 16 Mc/sec. EPR signals were recorded at 9.33 kMc/sec.

3. Results and discussion

3.1 DSC

The crystallographic phase transitions in KMnF_3 and TiMnCl_3 are known to occur at 186 K and 303 K respectively with c/a ratio in the tetragonal modification very close to unity in both. KMnF_3 (Minkiewicz *et al* 1970) has $c/a=1.007$ at 95 K and TiMnCl_3 (Melamud *et al* 1971, Kestigian 1970) has $c/a=1.004$ below 300 K. Neutron diffraction technique failed to detect these small distortions (Melamud *et al* 1971). The DSC measurements are very useful in detecting and ascertaining the order of a phase transition (Karkhanavala and Rao 1971). With this view these measurements were undertaken. The DSC run on TiMnCl_3 is shown in figure 1 a. The strikingly excellent sensitivity of DSC to pick up the very small distortion in TiMnCl_3 is evident. The heat of transition ΔH is 10 cal mole⁻¹. The transition appears to be first order. ΔH obtained for KMnF_3 by DSC is 2 cal mole⁻¹. Figure 1 b shows a DSC run for KMnF_3 also. Earlier Deenadas *et al* (1966) observed two anomalies at 83 K and 179 K (with a sample of 46.7 g) in their specific heat measurements of KMnF_3 . The lower temperature peak, corresponding to the magnetic transition, was relatively sharp while the high temperature anomaly, attributed to the crystallographic phase transition, was about 20 K wide. This indicates that the crystallographic phase transition is second order. More recently Hirakawa and Furukawa (1970) measured the specific heat (on arbitrary scale) of KMnF_3 (2 g sample) with a sensitive calorimeter in the neighbourhood of the crystallographic transition. They obtained a very sharp (total span 0.5 K) anomaly at 186.6 K with a small but finite temperature hysteresis confirming it to be a first order transition. Our results on 80 mg sample of KMnF_3 are in agreement with this observation. The value of the transition temperature T_t obtained by us is 184 K. We could not check

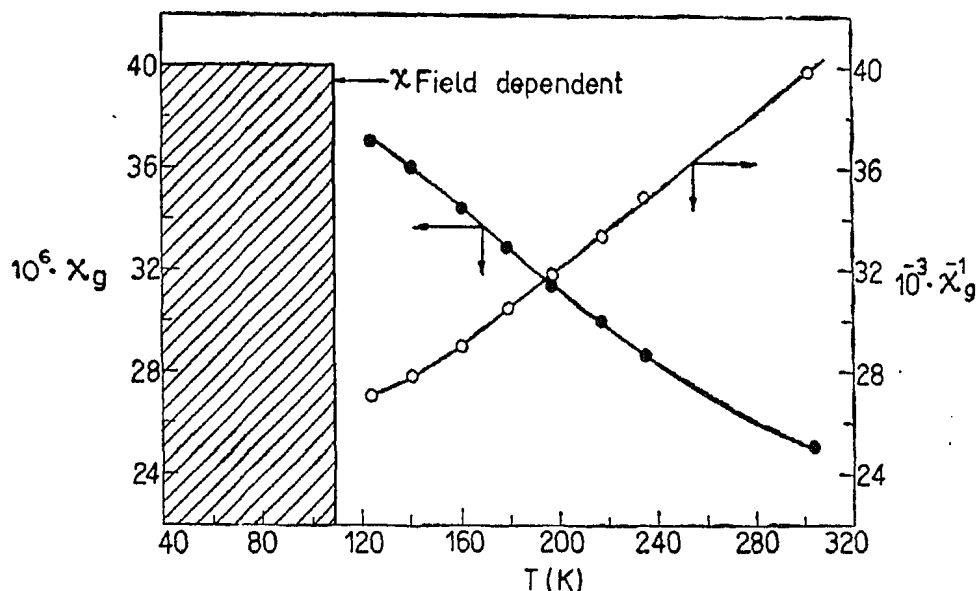


Figure 2. Magnetic susceptibility and inverse susceptibility as a function of absolute temperature of polycrystalline TlMnCl_3

the hysteresis in T_t of KMnF_3 since our instrument does not give a satisfactory programmed cooling below 190 K at $4^\circ/\text{min.}$ rate at which we obtained the best signal on heating. The ΔH values for both of these compounds, reported here for the first time, are unusually low.

As observed in our DSC results, there is a definite hysteresis of about 5 K in T_t during heating and cooling runs of TlMnCl_3 . We conclude that in TlMnCl_3 also, as in KMnF_3 , this crystallographic transition is first order. We could not extend our DSC study to cover the magnetic transitions in these compounds since the lower limit of temperature in our instrument is 175 K.

3.2 Magnetic susceptibility

We measured the susceptibility of TlMnCl_3 powder from 95 to 300 K. The results are shown in figure 2. Above 160 K, the system obeys Curie-Weiss law with an extrapolated Curie temperature of -231 K. The trend in deviation of susceptibility from Curie-Weiss law below 160 K indicates an antiferromagnetic ordering. The magnetic data on both KMnF_3 (Ogawa 1959) and TlMnCl_3 are given in table 1.

Table 1. Magnetic data of the two compounds TlMnCl_3 and KMnF_3 . μ^\dagger eff and μ^\ddagger eff are the values of effective magnetic moment of Mn^{2+} ions as determined by susceptibility and neutron diffraction measurements respectively.

No	Compound	Curie constant	μ^\dagger eff (BM)	Paramagnetic Curie temp. (θ) (K)	μ^\ddagger eff (BM)
1	TlMnCl_3	4.89 ^a	6.25 ^a	-231 ^a	4.70 ^b
2	KMnF_3	4.52 ^c	6.04 ^c	-203 ^c	5.06 ^d

^a present magnetic susceptibility data; ^b Melamud *et al* (1971);

^c Ogawa (1959); ^d Scatturin *et al* (1961)

3.3 *NMR and EPR*

In TlMnCl_3 the paramagnetic shifts of Tl^{203} and Tl^{205} at room temperature are found to be small ($\sim 0.04\%$) and positive. These shifts in all perovskites of the ABF_3 type, measured at the monovalent site, are large and negative. In ABF_3 perovskites the cell dimension is about 4.2 \AA , whereas in TlMnCl_3 it is 5.02 \AA . It appears that the change in cell dimension is responsible for this kind of behaviour. The line width of thallium resonance remains unchanged as the T_N is approached from the paramagnetic state. The paramagnetic shift of thallium resonance did not change appreciably with temperature (the change in the shifts were within experimental errors) and thus no definite relation could be established between the shift and temperature. One would expect a Curie-Weiss relation in this case also. The signal disappeared just below the Neel temperature which is in conformity with such observation in many other antiferromagnets. The thallium resonance shape was insensitive to the crystallographic phase change as the spin of both its isotopes is $\frac{1}{2}$. Also there was no anomalous change in the paramagnetic shift on crossing the temperature of this transition T_t .

There was no report available in literature on K^{39} NMR in KMnF_3 .^{*} During the course of this work it was felt worthwhile to study K^{39} NMR in KMnF_3 . The salient features of our NMR studies on a single crystal of KMnF_3 are as follows. The room temperature paramagnetic shift of K^{39} NMR is -0.15% . The NMR signal was followed as a function of temperature upto the crystallographic transition temperature $T_t (=186 \text{ K})$. From these measurements, however, no definite relationship between the paramagnetic shift and the temperature could be established. This is partly because of our experimental uncertainties. The signal below T_t became too weak to be followed upto T_N . This reduction in intensity is expected since due to the quadrupole

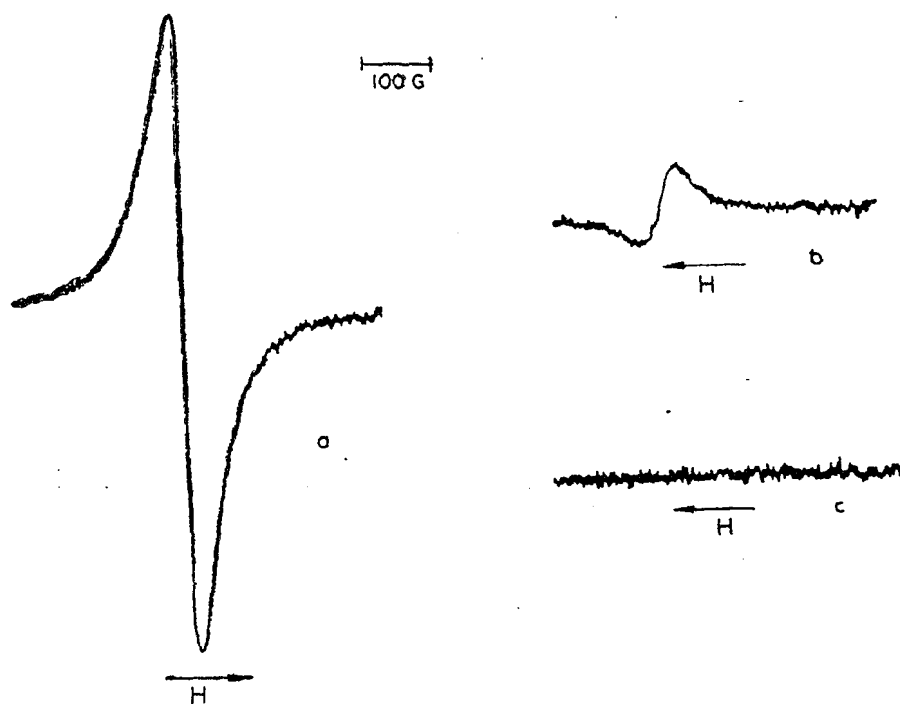


Figure 3. EPR spectra of Mn^{2+} in polycrystalline TlMnCl_3 in the neighbourhood of its T_N . (a) at 118K, (b) at 116K and (c) at 114K

^{*}During the period when this report was being prepared for publication, the authors came across the recent work of Borsa (1973) on NMR of K^{39} in KMnF_3 . The room temperature measurements presented here are in fair agreement with those presented in his work.

Table 2. Crystallographic (T_t) and the magnetic (T_N) transition temperatures of $TlMnCl_3$ and $KMnF_3$ as determined by different techniques.

No	Compound	Trans. temp.	Techniques					
			X-ray	Sp. ht.	DSC	NMR (K)	ESR	Mag. Sus.
1	$TlMnCl_3$	T_t	303	—	300.5 ^a	N.O.	N.O.	N.O.
		T_N	N.O.	—	N.O.	118 ^a	115 ^a	120
2	$KMnF_3$	T_t	184	186.6	184 ^a	186 ^a	N.O.	N.O.
		T_N	N.O.	83	N.O.	N.O.	88 ^b	82 ^c

N.O. not observed; ^a Present work; ^b Gupta *et al* (1972);
^c For two different samples of $KMnF_3$, two different values of T_N one reported by Ogawa (1959). For a more recent value of T_N , determined by χ -measurements, see Heeger *et al* (1961)

interaction in the tetragonal phase, the three transitions $3/2 \rightarrow 1/2$, $1/2 \rightarrow -1/2$ and $-1/2 \rightarrow -3/2$ would be split in a general orientation. There would be a further reduction of intensity due to domain formation in the crystal.

The Mn^{2+} EPR measurements were done on polycrystalline samples of $TlMnCl_3$ in the temperature range 77-400 K. The principal observations are as follows: (Vijayaraghavan *et al* 1972)

- (i) The g value at room temperature was close to that of a free electron;
- (ii) There was no measurable effect on g value in the neighbourhood of the crystallographic transition; and
- (iii) The EPR signal observed at selected temperatures for $TlMnCl_3$ is shown in figure 3. It disappeared at 115 K. The EPR line was exchange narrowed as was the case in $KMnF_3$ (Gulley *et al* 1969).

The temperatures of the crystallographic and magnetic phase transitions in $TlMnCl_3$ measured by different techniques along with those in $KMnF_3$ are given in table 2.

4. Conclusion

The compounds $TlMnCl_3$ and $KMnF_3$ exhibit very similar physical properties. The heats of crystallographic transitions are unusually low and these transitions are first order. The paramagnetic shift of thallium resonance is small and positive whereas that of K^{39} is negative. The paramagnetic Curie temperature, as deduced from magnetic susceptibility data on $TlMnCl_3$ is -231 K. The corresponding one for $KMnF_3$ reported in literature is -203 K. The crystallographic transition in $TlMnCl_3$ could not be detected by EPR, NMR and magnetic susceptibility techniques. However, it was possible to locate it with ease by DSC.

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