Crystallographic and magnetic phase transition in TiMnCl₃

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Abstract. The results of our NMR, EPR and magnetic susceptibility measurements in the paramagnetic state of TiMnCl₃ are reported here. The NMR paramagnetic shift of thallium is found to be small but positive. Mn²⁺ EPR line is exchange narrowed. The susceptibility measurements indicate an antiferromagnetic transition. The heat of crystallographic phase transition ΔH in TiMnCl₃ 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 KMnF₃ ΔH, which is reported here for the first time, is determined to be 2 cal mole⁻¹.

Keywords. Phase transition, antiferromagnetic; differential scanning calorimetry; TiMnCl₃; KMnF₃

1. Introduction

Many ionic compounds of the ABX₃ type crystallise in the perovskite structure in which B ions are situated in the holes created by close packing of AX₃ layers. TiMnCl₃ 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 TiMnCl₃ and KMnF₃, another member of the ABX₃ perovskite family. Both undergo a cubic → tetragonal crystallographic phase transition, believed to be due to the softening of the Γ₅₅ phonon mode. The magnetic ions (Mn²⁺) 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. KMnF₃ 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 F¹⁹ and Mn⁵⁸), etc. On the other hand, no results of the NMR, EPR, susceptibility and heat of transition measurements are available for TiMnCl₃. In this paper, we present the results of our measurements on TiMnCl₃ and KMnF₃.

2. Preparation

The sample of polycrystalline TiMnCl₃ was made by heating equimolar quantities of TiCl and MnCl₂ · 4H₂O in a stream of dry Cl₂ gas instead of HCl (Kestigian 1970). An
Figure 1. DSC Scans of (a) TlMnCl₃ (132 mg) and (b) KMnF₃ (80 mg)

orange coloured lump was obtained. TlMnCl₃ was always handled in a drybox under dry nitrogen. The cell-constants of a single crystal grown from this powder of TlMnCl₃ agreed very well with those reported in literature. Chips of single crystal KMnF₃ 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 KMnF₃ and TlMnCl₃ 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. KMnF₃ (Minkiewicz et al 1970) has \( c/a = 1·007 \) at 95 K and TlMnCl₃ (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 TlMnCl₃ is shown in figure 1 a. The strikingly excellent sensitivity of DSC to pick up the very small distortion in TlMnCl₃ is evident. The heat of transition \( \Delta H \) is 10 cal mole⁻¹. The transition appears to be first order. \( \Delta H \) obtained for KMnF₃ by DSG is 2 cal mole⁻¹. Figure 1 b shows a DSC run for KMnF₃ 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 KMnF₃. 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 KMnF₃ (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 KMnF₃ are in agreement with this observation. The value of the transition temperature \( T_t \) obtained by us is 184 K. We could not check
the hysteresis in $T_t$ of KMnF$_3$ since our instrument does not give a satisfactory programmed cooling below 190 K at 4°/min. rate at which we obtained the best signal on heating. The $\Delta H$ 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 TiMnCl$_3$. We conclude that in TiMnCl$_3$ 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 TiMnCl$_3$ 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 TiMnCl$_3$ are given in table 1.

![Figure 2. Magnetic susceptibility and inverse susceptibility as a function of absolute temperature of polycrystalline TiMnCl$_3$](image)

<table>
<thead>
<tr>
<th>No</th>
<th>Compound</th>
<th>Curie constant</th>
<th>$\mu^\dagger$ eff (BM)</th>
<th>Paramagnetic Curie temp. (K)</th>
<th>$\mu^\ddagger$ eff (BM)</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>TiMnCl$_3$</td>
<td>4.89$^a$</td>
<td>6.25$^a$</td>
<td>$-231^a$</td>
<td>4.70$^b$</td>
</tr>
<tr>
<td>2</td>
<td>KMnF$_3$</td>
<td>4.52$^c$</td>
<td>6.04$^c$</td>
<td>$-203^c$</td>
<td>5.06$^d$</td>
</tr>
</tbody>
</table>

$^a$ present magnetic susceptibility data; $^b$ Melamud et al (1971); $^c$ Ogawa (1959); $^d$ Scatturin et al (1961)
3.3 NMR and EPR

In $\text{TlMnCl}_3$ the paramagnetic shifts of $^{203}\text{Tl}$ and $^{205}\text{Tl}$ at room temperature are found to be small ($\sim 0.04\%$) and positive. These shifts in all perovskites of the $\text{ABF}_3$ type, measured at the monovalent site, are large and negative. In $\text{ABF}_3$ perovskites the cell dimension is about 4.2 Å, whereas in $\text{TlMnCl}_3$ it is 5.02 Å. 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 $^{39}\text{K}$ NMR in $\text{KMnF}_3$. During the course of this work it was felt worthwhile to study $^{39}\text{K}$ NMR in $\text{KMnF}_3$. The salient features of our NMR studies on a single crystal of $\text{KMnF}_3$ are as follows. The room temperature paramagnetic shift of $^{39}\text{K}$ NMR is $-0.15\%$. The NMR signal was followed as a function of temperature up to the crystallographic transition temperature $T_t (=186$ 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 up to $T_N$. This reduction in intensity is expected since due to the quadrupole

![Figure 3. EPR spectra of Mn$^{2+}$ in polycrystalline $\text{TlMnCl}_3$ in the neighbourhood of its $T_N$. (a) at 118K, (b) at 116K and (c) at 114K.](image)

*During the period when this report was being prepared for publication, the authors came across the recent work of Borsa (1973) on NMR of $^{39}\text{K}$ in $\text{KMnF}_3$. 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 TIMnCl$_3$ and KMnF$_3$ as determined by different techniques.

<table>
<thead>
<tr>
<th>No</th>
<th>Compound</th>
<th>Trans. temp.</th>
<th>Techniques</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$T_t$ (K)</td>
<td>X-ray</td>
</tr>
<tr>
<td>1</td>
<td>TIMnCl$_3$</td>
<td>303</td>
<td>N.O.</td>
</tr>
<tr>
<td></td>
<td>$T_N$</td>
<td>N.O.</td>
<td>N.O.</td>
</tr>
<tr>
<td>2</td>
<td>KMnF$_3$</td>
<td>184</td>
<td>N.O.</td>
</tr>
</tbody>
</table>

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 x-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$^{4+}$ EPR measurements were done on polycrystalline samples of TIMnCl$_3$ 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 TIMnCl$_3$ 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 TIMnCl$_3$ measured by different techniques along with those in KMnF$_3$ are given in table 2.

4. Conclusion

The compounds TIMnCl$_3$ 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 TIMnCl$_3$ is $-231$ K. The corresponding one for KMnF$_3$ reported in literature is $-203$ K. The crystallographic transition in TIMnCl$_3$ 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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References

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