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# Cubic–tetragonal transition in $\text{KMnF}_3$ : IR hard-mode spectroscopy and the temperature evolution of the (precursor) order parameter

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## Abstract

Precursor effects were observed in  $\text{KMnF}_3$  using infrared hard-mode spectroscopy. The intensity of the infrared-active mode near  $265 \text{ cm}^{-1}$  follows the thermodynamic order parameter,  $Q$ , in the tetragonal phase ( $I4/mcm$ ). An additional weak signal is found in the cubic phase ( $Pm\bar{3}m$ ). The order parameter step at  $T_o = 185.95 \text{ K}$  ( $L = 0.129 \text{ J g}^{-1}$ ) is smeared with excess intensity due to the tetragonal short range order extending to  $T > 215 \text{ K}$ . The intensity follows the predictions of Landau theory with a defect field  $G_{\text{defect}} = -hQ$ ,  $h = 6 \text{ J mol}^{-1}$ . The observed excess intensities are compared with the appearance of precursor elastic softening. It is concluded that the precursor softening and the local tetragonal short range order are likely to be related to an extended defect structure, such as a tweed pattern, which may be stabilized by extrinsic defects.

(Some figures in this article are in colour only in the electronic version)

## 1. Introduction

The phase transitions in  $\text{KMnF}_3$  and the related compounds  $\text{KMn}_{1-x}\text{Ca}_x\text{F}_3$  have been thoroughly investigated since 1967 [1–10]. The cubic/tetragonal transition  $Pm\bar{3}m$ – $I4/mcm$  occurs at 186.04 K on heating and 185.95 on cooling [11]. This transition has been analysed thermodynamically in great detail [11, 12] with little disagreement with various previous results (except for an attempt to quantify the transition as Ising-like in [7]). The transition is first order with a latent heat  $L = 0.129(2) \text{ J g}^{-1}$  [11, 12]. The character of the transition and the symmetry of the order parameter are very similar to isostructural  $\text{SrTiO}_3$  [13–15].

The order parameter of the cubic/tetragonal transition of  $\text{KMnF}_3$  was determined from diffraction experiments and from specific heat measurements [11, 12] and was shown to follow mean-field behaviour with a Landau potential in the high temperature approximation:

$$\Delta G = \frac{1}{2}2.781(T - 185.76)Q^2 - \frac{1}{4}57.63Q^4 + \frac{1}{6}574.2Q^6 + \frac{1}{2}g(\text{grad}Q)^2 \quad (1)$$

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where the energy is measured in  $\text{J mol}^{-1}$  and the temperature in K. The quantum saturation could not be determined [14, 16] because other phase transitions occur before the order parameter of the cubic/tetragonal transition reaches the quantum regime. The Ginzburg parameter, which measures the resistance of the crystal to form domain boundaries, is also unknown because the thickness of twin boundaries in the tetragonal phase has not been measured. The wall thicknesses in oxide materials are of the order of 0.5–4 nm at low temperatures [17–28] while martensites have smaller length scales of approx. 0.5 nm [29]. The equivalent surface energies are typically  $4 \times 10^{-3} \text{ J m}^{-2}$  [30, 31]. The value of the Ginzburg parameter  $g$  is then estimated to be of the order of  $4 \times 10^{-15} \text{ J m}^2 \text{ mol}^{-1}$ . The stepwise character of the transition was already seen in Raman spectroscopy in 1974 [3] and described as being due to fluctuations. Similarly, Gibaud *et al* [5] observed the step of the spontaneous strain near the transition point but analysed the data with an overall ‘critical’ power law; the same step was already discussed by Cox *et al* [32]. The weakly first-order transition leads to a small latent heat and very careful measurements of the heat capacity are needed to quantify the step of the order parameter

at  $T_0$  [11, 12, 33, 34]. Importantly, not only the latent heat was observed but also avalanches during the transition [35] as shown by random exothermic heat fluxes during the latent heat measurements in [11]. In Na-doped samples a tendency to form glass-like states was observed [8] similar to the results from Ca-doped samples [36].

The question arises whether the macroscopically stepwise transition may, when observed on a local scale, also display a continuous phase transition. The tendency for a continuous transition is clearly demonstrated by doping  $\text{KMnF}_3$  with Ca. Romero *et al* [12] have shown that doping with 0.5 mol% Ca leads to a tricritical transition. This transition was found to follow mean-field behaviour macroscopically with a vanishing fourth-order term in the Landau potential in equation (1). Similarly, Stokka *et al* [37, 38] measured the specific heat under uniaxial stress and found a continuous transition at  $\sigma = 0.45$  kbar for [110] stress. It was conjectured, therefore, that short range order very close to the transition point would lead to an apparently continuous transition while the transition in the macroscopic, thermodynamic limit remains stepwise.

Short range order or fluctuations in the high temperature phase  $Pm\bar{3}m$  have also been seen in the measurement of elastic properties. Three-point bending experiments at low frequencies [36] and high frequency ultrasonic measurements [39] showed a decrease of the elastic moduli of  $\text{KMnF}_3$  at a temperature as much as 100 K above the transition point. Both sets of data are consistent when analysed as power law decay [36, 40]:

$$\Delta C/C_{250\text{ K}} = C_0[(T - T_0)/T_0]^{-K}. \quad (2)$$

The transition temperature  $T_0$  is 186.04 K on heating. The exponent  $K$  is  $0.5 \pm 0.1$  while only  $C_{44}$  showed a higher exponent with a large error bar. The amplitude  $C_0$  varied with frequency and showed higher values at high frequencies. This leads to the possibility that the origin of the short range order is dynamical. Indeed, low frequency Raman spectra (with the same symmetry as the moduli) by Kapusta *et al* [10] show the evolution of a central peak at temperatures above the transition point. Equivalent spectra in the infrared absorption of reflection would then show the degree of static disorder or any fluctuation with odd symmetry. It is the purpose of this paper to present the results of infrared hard-mode spectroscopy [41–46] of  $\text{KMnF}_3$  over a large temperature interval above and below the transition point. This is the first determination of the local order parameter using infrared spectroscopy in a fluorite system.

## 2. Experimental details

The  $\text{KMnF}_3$  sample used in this study was synthesized at University du Maine (Le Mans, France) using the Bridgman–Stockbarger method. The pure  $\text{KMnF}_3$  sample did not show any trace of calcium according to the chemical characteristics of the sample using an electron microprobe CAMECA SX50 [36].

Infrared powder pellet absorption technique was used to record infrared spectra of  $\text{KMnF}_3$ . Both KBr and polyethylene were used as matrix materials. Fine sample powders were

thoroughly mixed with the matrix powders and the mixtures were pressed into discs of 13 mm in diameter under vacuum. In order to reduce static charges caused by the mixing, a few drops of pentane were used for the mixing of the sample with polyethylene powder. The sample pellets were cooled to low temperatures using a closed-cycle liquid-helium cryostat (LEYBOLD) equipped with polyethylene windows.

Absorption spectra of  $\text{KMnF}_3$  were recorded using a Bruker 113v FT-IR spectrometer at temperatures between 25 and 300 K. The data recording was carried out under vacuum to avoid absorption from water and carbon oxides in the air. Experiments were performed in the region of approx. 350–700  $\text{cm}^{-1}$  using an HgCdTe detector cooled with liquid nitrogen and in the far-infrared, the region of 70–700  $\text{cm}^{-1}$ , using a room temperature DTGS detector. Instrumental resolution was 2  $\text{cm}^{-1}$ . Several runs of measurements were performed and the results were shown to be reproducible (figure 1). Data analysis and curve fitting were carried out using OPUS-IR (Bruker) and OriginPro 8 software.

## 3. Results and discussion

The analysis of the excess reflectivity of the IR spectra follows the rules of hard-mode spectroscopy [44] for modes which have irreducible representations different from those of the order parameter (the change of the mode frequency is also clearly visible in figure 2 but proved to be more difficult to fit quantitatively):

$$\Delta I = A Q^2 + B Q^4. \quad (3)$$

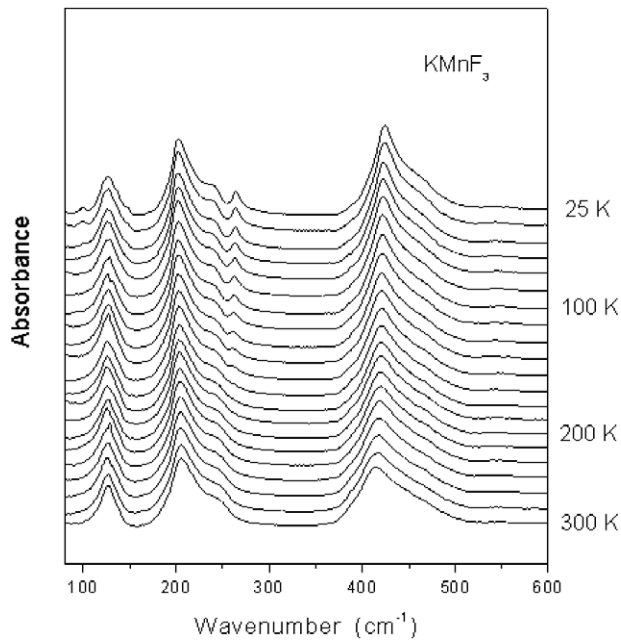
Assuming  $A \gg B$  the resulting  $Q^4$  function ( $\Delta I^2$ ) is scaled with respect to the known order parameter as determined by specific heat measurements and the analysis of the lattice distortion following from equation (1) via  $dG/dQ = 0$ :

$$Q^4 = \left( \frac{57.63 + \sqrt{3321.22 + 6387.4(185.76 - T)}}{1148.4} \right)^2. \quad (4)$$

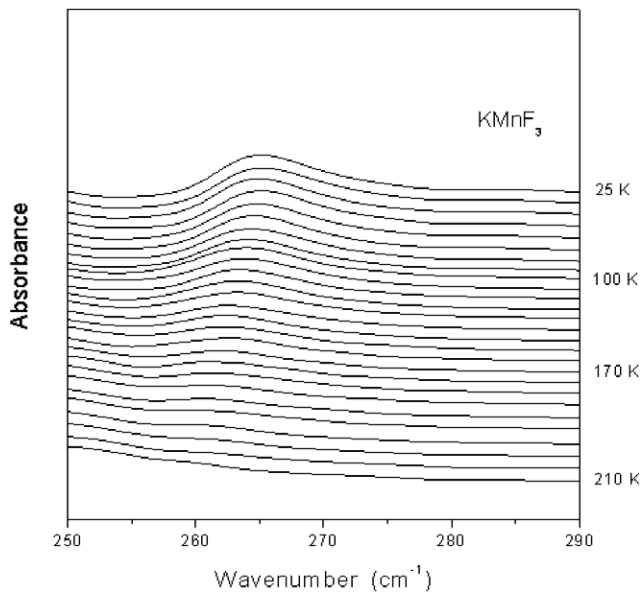
The resulting graph  $Q$  versus  $T$  in figure 3 shows that all experimental results are consistent at  $88\text{ K} < T < 186.04\text{ K}$ . The low temperature IR data are still close to the extrapolated  $Q(T/T_0)$  curve but details are changed by subsequent phase transitions below 88 K.

This result confirms  $A \gg B$  and shows that the chosen IR-active phonon intensity does indeed follow the temperature evolution of the static order parameter as given in equation (3).

We can now investigate the short range order as detected by the IR intensity at  $T > T_c$ . In figure 4 the temperature evolution of the excess intensity of the peak at 265  $\text{cm}^{-1}$  is shown. The jump of the order parameter at  $T_0$  is visible only in the strain and entropy data (equation (4)) while the transition is apparently continuous as seen by the infrared spectroscopic measurement. Short range order appears at  $T/T_c = 0.995$  and continues until above  $T/T_c = 1.16$  (215.5 K). This temperature interval is very similar to that where softening of the elastic moduli in  $\text{KMnF}_3$  is observed by Salje and Zhang [36] but significantly smaller than the interval where high frequency measurements show precursor softening. This

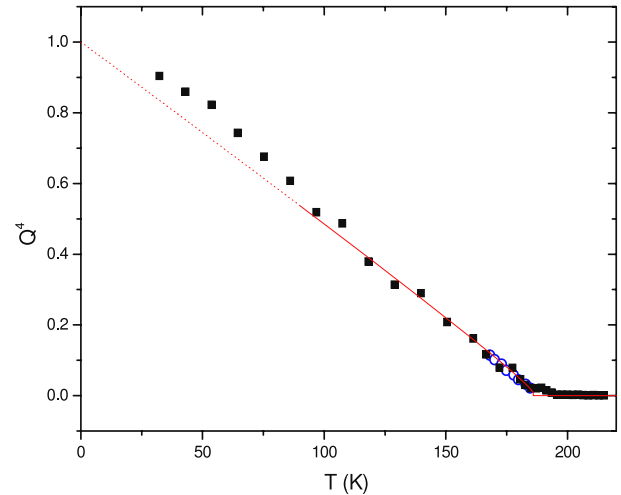


**Figure 1.** Infrared absorption spectra of  $\text{KMnF}_3$  between 25 K and room temperature. Note the peak near  $265\text{ cm}^{-1}$ , which is indicative of the phase transitions and used for hard-mode spectroscopy. The temperatures for the individual measurements in figure 1 are 25, 40, 60, 70, 80, 90, 100, 120, 140, 150, 160, 170, 180, 190, 200, 210, 220, 240, 260, 280 and 300 K.

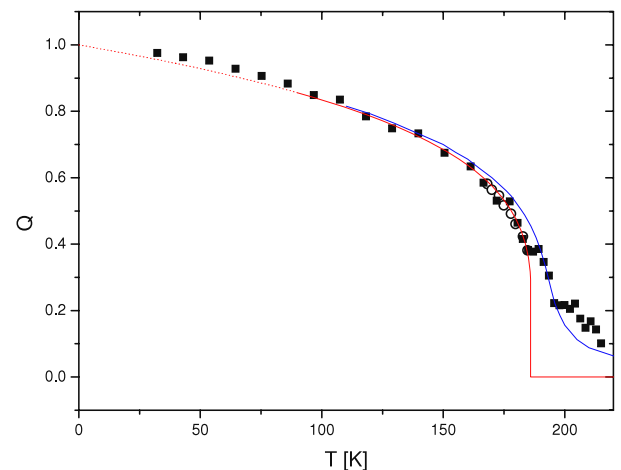


**Figure 2.** Details of the peak near  $265\text{ cm}^{-1}$ . The peak position and the peak intensity reflect the temperature evolution of the structural order parameter in  $\text{KMnF}_3$ . The peak intensity is used in the quantitative analysis. The mode frequency softens under heating and shows qualitatively the same temperature dependence as the peak intensity.

rules out any resonance phenomenon which would be close to phonon frequencies. Lower frequency excitations, well below the phonon range, would explain our observations. The values of the exponent  $K$  indicate that such fluctuations occur in three



**Figure 3.** Temperature evolution of the excess intensity of the  $265\text{ cm}^{-1}$  line (dots) and the comparison with the order parameter of the  $Pm\bar{3}m-I4/mcm$  as determined by calorimetric measurements [11, 12] shown as a line. Below 88 K another phase transition develops which shows weak coupling with the mode at  $265\text{ cm}^{-1}$ . Open circles are data from [11].



**Figure 4.** Temperature evolution of the order parameter of the transition  $Pm\bar{3}m-I4/mcm$  in  $\text{KMnF}_3$ . The data points represent the excess intensity of the  $265\text{ cm}^{-1}$  mode, the lines with the abrupt change are the result of calorimetric measurements [11, 12] and measure the macroscopic order parameter, while the continuous line is the same Landau potential as the first-order transition but modified by a field term  $-hQ$  where the field strength is  $h = 6\text{ J mol}^{-1}$ . Open circles are data from [11]. The resolution of the order parameter determination by IR spectroscopy is 0.05 above  $T_0$  and 0.01 below  $T_0$ .

dimensions [40], which is compatible with the idea of low frequency rigid unit vibrations or dynamical tweed structures in the cubic phase [47]. These vibrations are not related to the actual soft modes but must be lower in frequency. Hatta *et al* [48] argued that the damping of ultrasonic modes in  $\text{KMnF}_3$  could be understood as an intrinsic phenomenon provided that the time constant of the damping was itself strongly temperature-dependent. Unfortunately, no experimental data were given so that it is impossible to compare their results with the later observations of precursor phenomena. A power

law fit by Hatta *et al* is not compatible with any of the more recent observations. Nevertheless, their characteristic time constant is of the order of  $10^{-9}$  s which lies within the range of possible relaxations observed in our experiments. This does not prove that the softening is related to the central peak or that the feature is intrinsic while such possibilities can also not be excluded for undoped crystals. A careful analysis of the elastic anomaly in the cubic phase of the structurally similar transition in SrTiO<sub>3</sub> by Hochli and Bruce [49] lead to a very different result. These authors found  $K = 1.5$  while other experimental data were quoted to range from 0.66 to 1.7. These authors argued that their values are not compatible with criticalities of standard theoretical models which would, for example, lead to values of 0.4 for the Heisenberg model. Defect-related anomalies, on the other hand, were expected to yield much larger values (e.g.  $K = 1.3$  for a Heisenberg model with relaxing point defects). The conclusion was reached that the anomaly has nothing to do with intrinsic criticalities but involves a dynamical process by which the local order is related to the motion of 90° microdomain walls, i.e. precursors to the observed twins. A similar argument was given by Andrews [50] who showed that the crystal imperfections are the likely reason for phenomena related to the central peak or defect-induced fluctuations. Salje and Zhang [36] argued that dynamical fluctuations—e.g. as small twin segments in all three crystallographic orientations or, more probably, tweed—are at the origin of the precursor softening of KMnF<sub>3</sub>. In addition, a small number of defects may stabilize the tweed at  $T > T_c$  and, hence, stabilize the precursor structure. Similarly, local symmetry breaking may be concluded from the Raman intensities at  $T > T_c$  observed by Kapusta *et al* [10]. Doping of KMnF<sub>3</sub> with Li leads to clearly visible (but broad) symmetry-forbidden Raman lines in the cubic phase. Data presented in this paper showed visible peaks at 700 K, which is clearly beyond any fluctuation or precursor softening regime reported in this paper. Undoped material, as used by Hayward *et al* [11], showed no such effects in the specific heat measurements where the latent heat is strictly limited to a small interval around  $T_0$ . Ca-doped material [12] showed field effects with excess latent heat at higher temperatures which were captured by a field term similar to the treatment in this paper. In summary, the infrared hard-mode spectroscopy shows local symmetry breaking in the high temperature phase while the overall symmetry remains  $Pm\bar{3}m$ . The temperature interval where this short range order is observed coincides with the regime of low frequency elastic softening. It is tempting, therefore, to conjecture that the local structure shows tetragonal or orthorhombic distortions on a nanometre scale while the averaged structure is  $Pm\bar{3}m$ . A possible geometrical configuration is the tweed microstructures, either as dynamical structures or as structures partly stabilized by extrinsic defects. Similar observations and simulations have been discussed in [51–53, 28, 54–59].

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