

## PRESSURE EFFECTS ON THE COOPERATIVE JAHN–TELLER DISTORTION IN $AMnF_4$ ( $A = Na, Tl$ )

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This work investigates the Optical Absorption spectrum of the  $AMnF_4$  layer perovskites of  $Mn^{3+}$ , and its variation with the pressure. We show that the crystal-field transition energies and their pressure shifts provide a very useful information about the local structural changes in the  $MnF_6^{3-}$  complex and how it changes with the pressure, once the correlations between crystal-field electronic structure and coordination geometry around  $Mn^{3+}$  has been established. Along this work we demonstrate that the equatorial and axial distances decrease from 1.844 to 1.813 Å, and from 2.167 to 2.090 Å, respectively, in the 0–100 kbar range, leading to a partial reduction of the Jahn–Teller distortion.

*Keywords:*  $Mn^{3+}$ ;  $MnF_6^{3-}$ ; Jahn–Teller effect; Pressure spectroscopy; Layer perovskite

### 1 INTRODUCTION

This work investigates the effect of pressure on the Jahn–Teller (JT) distortion of  $Mn^{3+}$  ions in the antiferrodistortive  $AMnF_4$  ( $A = Tl, Mn$ ) crystals through Optical Absorption (OA) spectroscopy. These systems are attractive for this purpose since a rich band structure associated with the spin-allowed transitions  ${}^5B_{1g} \rightarrow {}^5\Gamma_i$  ( $\Gamma_i = A_{1g}, B_{2g}$  and  $E_g$ ) and the spin-forbidden transitions,  ${}^5B_{1g} \rightarrow {}^3B_{1g}$ , are observed in the visible–UV range.

The aim of this research is to establish correlations between the variation of the crystal-field (CF) energies and the local structure around  $Mn^{3+}$ , which strongly depends on both, the volume and the JT distortion, displayed by the  $MnF_6^{3-}$  complex [1]. The knowledge of these correlations will allow us to elucidate whether the application of pressure gives rise to a release of the JT distortion, leading to the partial disappearance of the in-plane antiferrodistortive structure, or it induces out-of-plane tilts of the  $MnF_6^{3-}$  octahedra (Fig. 1). In addition, we would be able to extract information about local structural changes around  $Mn^{3+}$  under pressure from the OA spectra. This aspect is relevant since previous structural works under pressure performed on  $Mn^{3+}$  fluorides ( $AMnF_4$ ) did not succeed to detect variations of the Mn–F distances with the pressure using X-ray techniques [2, 3].

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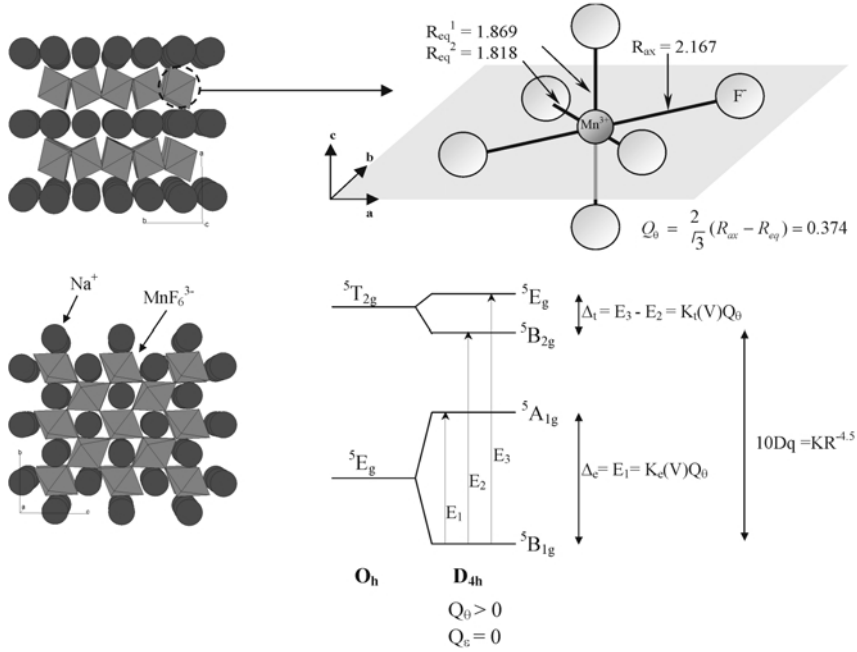


FIGURE 1 Crystal structure of NaMnF<sub>4</sub>, local structure around Mn<sup>3+</sup> and Crystal Field energy-state diagram for Mn<sup>3+</sup> in O<sub>h</sub> and D<sub>4h</sub> symmetries.

## 2 EXPERIMENT

The OA spectra upon pressure of the AMnF<sub>4</sub> (A = Tl, Na) samples were obtained using a specially designed spectrophotometer. The monochromatic light in the UV–VIS–IR range was obtained by means of Spectra Pro-300i ARC Monochromator and suitable filters. The light was chopped and detected with a Hamamatsu R-928 Phototube, and a SR 830 Lock-in amplifier. Pressure experiments were done in a Diamond Optics, Inc. DAC using single crystals of 100 × 150 × 40 μm<sup>3</sup>, which were immersed in paraffin oil as pressure transmitting media in order to avoid crystal hydration. The pressure in the hydrostatic cavity was calibrated from ruby chips. We used the 530.9 nm line of a Kr<sup>+</sup> ion laser (Coherent CR-500 K) for excitation.

## 3 RESULTS AND DISCUSSION

The CF spectrum of Mn<sup>3+</sup> ions in A<sub>n</sub>MnF<sub>n+3</sub> (A alkali ion; n = 1–3) can be understood on the basis of the JT distorted MnF<sub>6</sub><sup>3-</sup> complex unit [1]. The spectra of these compounds consist of three intense broad bands (named E<sub>1</sub>, E<sub>2</sub> and E<sub>3</sub> in Fig. 1), which are well resolved and located in the UV–Vis range. These bands are associated with electronic transitions between states of the same spin, S = 2. In addition, there are several narrow peaks corresponding to <sup>5</sup>B<sub>1g</sub> → <sup>3</sup>B<sub>1g</sub>. These electronic transitions are forbidden since they involve states of different spin. However, in these compounds they are partially allowed by the exchange mechanism [1]. In contrast to these spin-flip transitions, which are weakly CF dependent, the energy of the broad bands is very sensitive to distortions of the coordination geometry. Structural correla-

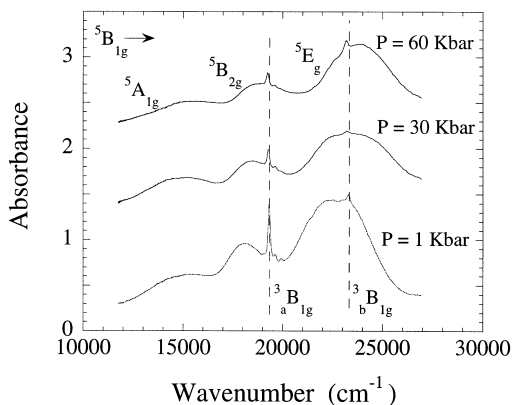


FIGURE 2 Optical absorption spectra of NaMnF<sub>4</sub> as a function of pressure.

tions performed on Mn<sup>3+</sup> fluorides [1, 4], indicate that the tetragonal splitting associated with the parent octahedral  $e_g$  and  $t_{2g}$  orbitals, termed  $\Delta_e = E_1$  and  $\Delta_t = E_3 - E_2$ , respectively, is proportional to the JT distortion, which is characterised by the  $Q_\theta$  normal coordinate in MnF<sub>6</sub><sup>3-</sup> complexes with local D<sub>4h</sub> symmetry [1, 4, 5]. On the other hand,  $E_2$  depends only on the equatorial Mn–F distance,  $R_{eq}$ , thus this transition is a very sensitive probe to detect variations of  $R_{eq}$  upon pressure.

Figure 2 shows the OA spectrum of NaMnF<sub>4</sub> and its variation with the pressure. At ambient conditions the three  $E_1$ ,  $E_2$  and  $E_3$  bands appear at 15450, 18250 and 22720 cm<sup>-1</sup>, respectively. The CF energies as well as the corresponding JT splitting,  $\Delta_e = 15450$  cm<sup>-1</sup> and  $\Delta_t = 4480$  cm<sup>-1</sup>, reflect nearly the D<sub>4h</sub> JT distortion of the MnF<sub>6</sub><sup>3-</sup> characteristic of a 2D layered perovskite AMnF<sub>4</sub> (A = K, Rb, Cs, Tl) [1] with a distortion  $Q_\theta = 0.374$  Å. The O<sub>h</sub> normal coordinate is derived from the equatorial and axial distances, obtained from X-ray diffraction:  $R_{eq} = 1.844$  Å and  $R_{ax} = 2.167$  Å, respectively [6].

The effect of applying pressure to this compound is mainly to shift the three intense bands towards higher energies, whereas a slight redshift is observed for the two spin-flip  ${}^5B_{1g} \rightarrow {}^3B_{1g}$  peaks. The variation of  $E_1$ ,  $E_2$  and  $E_3$  shows a linear behaviour with the pressure. The associated linear least-square fits for the three CF transitions are shown in Figure 3.

From these results, we are able to extract valuable information on the local structural changes around Mn<sup>3+</sup> under pressure, provided that we know how  $E_1$ ,  $E_2$  and  $E_3$  depend

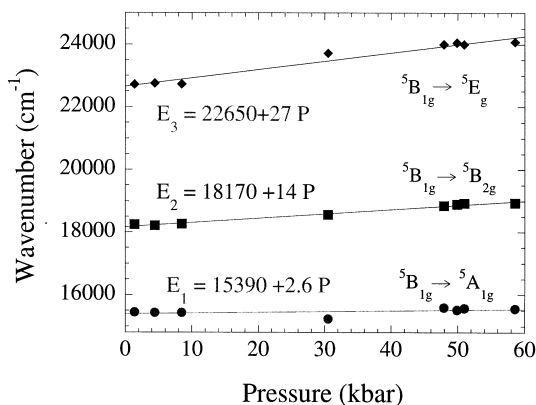


FIGURE 3 Variation of  $E_1$ ,  $E_2$  and  $E_3$  with pressure. Lines correspond to least-square linear fits.

on  $R_{\text{eq}}$  and  $R_{\text{ax}}$  (or  $R_{\text{eq}}$  and  $Q_\theta$ ). The use of the  $Q_\theta$  normal coordinate is important since the JT splittings,  $\Delta_e$  and  $\Delta_t$ , are both proportional to  $Q_\theta$  for slight deviations of the  $O_h$  symmetry [1, 5]:

$$\begin{aligned}\Delta_e &= K_e(V) \cdot Q_\theta \\ \Delta_t &= K_t(V) \cdot Q_\theta\end{aligned}\quad (1)$$

$K_e$  and  $K_t$  are the JT electron-lattice coupling parameters that, in general, should depend on the crystal volume. It must be pointed out that structural correlations performed along a series of  $\text{Mn}^{3+}$  fluorides [1], indicate that  $\Delta_e = 41780 Q_\theta$  and  $\Delta_t = 10700 Q_\theta$  (units in  $\text{cm}^{-1}$  and  $\text{\AA}$ ), with a ratio  $\Delta_e/\Delta_t \approx 3.9$  at ambient conditions. Note that the observed  $\Delta_e$  and  $\Delta_t$  values in the  $\text{NaMnF}_4$  are in good agreement with this figure.

Interestingly, the energy  $E_2$ , which is related to  ${}^5\text{B}_{1g} \rightarrow {}^5\text{B}_{2g}$  transition, depends and can be expressed as a function of  $R_{\text{eq}}$  as  $E_2 = K \cdot R_{\text{eq}}^{-n}$  [1, 8]. From this equation we can estimate the variation of  $R_{\text{eq}}$  with the pressure using  $n = 4.5$  [7]. Therefore, from pressure shifts of Figure 3, we conclude:

- (1) The equatorial Mn–F distance,  $R_{\text{eq}}$ , decreases upon pressure as it is clearly evidenced by the blue-shift of  $E_2$ :  $\partial E_2/\partial P = 14 \text{ cm}^{-1}/\text{kbar}$ .
- (2) The variation of  $R_{\text{eq}}$  with the pressure is given by  $\partial E_2/\partial P = (\partial E_2/\partial R_{\text{eq}})(\partial R_{\text{eq}}/\partial P)$  with

$$\frac{\partial E_2}{\partial R_{\text{eq}}} = -n \frac{E_2}{R_{\text{eq}}} = -4.5 \frac{18450}{1.844} = -45100 \text{ cm}^{-1}/\text{\AA} \quad (2)$$

So that we obtain  $\partial R_{\text{eq}}/\partial P = -14/45100 = -3.1 \times 10^{-4} \text{ \AA}/\text{kbar}$  what means a variation from ambient pressure to 100 kbar of  $\Delta R_{\text{eq}} = -0.031 \text{ \AA}$ .

- (3) This spectroscopic procedure provides a suitable method for deriving bond-distances variation that actually improves the XAS sensitivity. By using Eq. 2, we obtain a bond-distance accuracy of  $10^{-3} \text{ \AA}$  for a transition energy accuracy of  $50 \text{ cm}^{-1}$ , which is easy to accomplish through OA spectroscopy.
- (4) The JT distortion does not change significantly upon pressure. This conclusion is supported by the fact that a disappearance of the JT effect yielding  $Q_\theta \approx 0$  should induce a closure of the splitting associated with the  ${}^5E_g$  and  ${}^5T_{2g}$  states:  $\Delta_e = 0$  and  $\Delta_t = 0$ . On the contrary, we observe that  $\Delta_e$  and  $\Delta_t$  increase 260 and 1300  $\text{cm}^{-1}$ , respectively, on passing from ambient pressure to 100 kbar. Note that the variation of  $\Delta_t$  in the same pressure range is five times the variation of  $\Delta_e$  (Fig. 3).
- (5) The fact that  $\partial \Delta_e(P)/\partial P = 2.6 \text{ cm}^{-1}/\text{kbar}$  and  $\partial \Delta_t(P)/\partial P = 13 \text{ cm}^{-1}/\text{kbar}$  indicates a different behaviour for  $\Delta_t(P)$  and  $\Delta_e(P)$ , implying necessarily that  $K_e$  and  $K_t$  must both increase with pressure:  $\Delta K_e < \Delta K_t$ .

The relation between these electron-lattice coupling parameters and the crystal volume can be expressed as follows:

$$\begin{aligned}K_e(V) &= K_e^0 \cdot V^{-n_e/3} \\ K_t(V) &= K_t^0 \cdot V^{-n_t/3}\end{aligned}\quad (3)$$

The pressure results of Figures 2 and 3 can be reasonably explained in the framework of the JT model using values  $n_e = 3$  and  $n_t = 6$ .

Although the value of the exponents does not affect considerably the quantitative conclusion of this work, this particular choice is based on the two following facts:

- (1) The pressure derivatives of the JT electron-lattice coupling parameter are similar:  $\partial K_e/\partial P \approx \partial K_t/\partial P$ . This assumption is based on previous studies on the variation of the wave function coefficients  $N_t$  and  $N_e$  associated with the  $e_g$  and  $t_{2g}$  orbitals with the pressure:  $\partial N_e/\partial P \approx \partial N_t/\partial P$  [9].
- (2) A structural constraint from Eq. 1 requires that  $\Delta_e(P)/K_e(P) = \Delta_t(P)/K_t(P)$  for a given tetragonal distortion,  $Q_\theta$ . This means that for small departures from the O<sub>h</sub> symmetry

$$\frac{1}{K_e^0} \frac{\partial K_e}{\partial P} - \frac{1}{\Delta_e^0} \frac{\partial \Delta_e}{\partial P} = \frac{1}{K_t^0} \frac{\partial K_t}{\partial P} - \frac{1}{\Delta_t^0} \frac{\partial \Delta_t}{\partial P}.$$

So that we obtain values  $\partial K_e/\partial P \approx \partial K_t/\partial P = 70 \text{ cm}^{-1}/\text{\AA}/\text{kbar}$  using a bulk modulus  $B_0 = 600 \text{ kbar}$  [2] and the pressure derivatives given in Figure 3. This means that the electron-lattice coupling at 100 kbar is  $K_e(100) = 49300 \text{ cm}^{-1}/\text{\AA}$  and  $K_t(100) = 17400 \text{ cm}^{-1}/\text{\AA}$  and consequently the D<sub>4h</sub> distortion at 100 kbar is:

$$Q_\theta = \frac{\Delta_e(100)}{K_e(100)} = \frac{15710}{49300} \approx \frac{\Delta_t(100)}{K_t(100)} = \frac{5770}{17400} = 0.325 \text{ \AA}.$$

Therefore, the application of pressure induces a reduction of the tetragonal distortion from 0.374 Å at ambient pressure to 0.325 Å at 100 kbar:  $\Delta Q_\theta = -0.049 \text{ \AA}$ . In terms of bond distances, there is a reduction of  $R_{\text{eq}}$  and  $R_{\text{ax}}$ : from 1.844 to 1.813 Å for  $R_{\text{eq}}$  and from 2.167 to 2.094 Å for  $R_{\text{ax}}$ , which means  $\Delta R_{\text{eq}} = -0.031 \text{ \AA}$  and  $\Delta R_{\text{ax}} = -0.073 \text{ \AA}$  in the 0–100 kbar range.

In conclusion, the effect of pressure is mainly to reduce all Mn–F distances of the  $\text{MnF}_6^{3-}$ . The axial distance reduces 2.5 times the equatorial distance thus leading to a partial reduction of the JT distortion. This important result is in agreement with previous findings in the antiferrodistortive  $[\text{C}_3\text{H}_7\text{NH}_3]_2\text{CuCl}_4$  crystal using XRD and EXAFS under pressure [10], as well in the manganite  $\text{LaMnO}_3$  using neutron diffraction under pressure [11].

A salient feature is the increase of the electron-lattice coupling related to the JT effect with the pressure. Finally, we note that, from the proposed structural variation, the  $\text{MnF}_6^{3-}$  complex ( $B_{\text{local}} = 1420 \text{ kbar}$ ) is less compressible than the bulk crystal thus suggesting the existence of  $\text{MnF}_6^{3-}$  tilts upon pressure, in agreement with findings in  $\text{A}_2\text{CuCl}_4$  [10] and in  $\text{AMnF}_4$  [2].

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