The Jahn-Teller active fluoroperovskites $\text{ACrF}_3$ $A = \text{Na}^+, \text{K}^+$: thermo- and magneto-optical correlations as function of the A-site

F. L. M. Bernal, F. Lundvall, S. Kumar, P-A. Hansen, D. S. Wragg, and H. Fjellvåg
Centre for Material Science and Nanotechnology, University of Oslo, NO-0315, Norway

O. M. Løvvik
Department of Physics, University of Oslo, NO-0315, Norway and Sintef Industry, 0314 Oslo, Norway

Chromium (II) fluoroperovskites $\text{ACrF}_3 (A= \text{Na}^+, \text{K}^+)$ are strongly correlated Jahn-Teller active materials at low temperatures. In this paper, we examine the role that the A-site ion plays in this family of fluoroperovskites using both experimental methods (XRD, optical absorption spectroscopy and magnetic fields) and DFT simulations. Temperature-dependent optical absorption experiments show that the spin-allowed transitions $E_2$ and $E_3$ only merge completely for $A= \text{Na}$ at 2 K. Field-dependent optical absorption measurements at 2 K show that the oscillating strength of the spin-allowed transitions in NaCrF$_3$ increases with increasing applied field. Direct magneto-structural correlations which suppress the spin-flip transitions are observed for KCrF$_3$ below its Neél temperature. In NaCrF$_3$ the spin-flip transitions vanish abruptly below 9 K revealing magneto-optical correlations not linked to crystal structure changes. This suggests that as the long range ordering is reduced local JT effects in the individual CrF$_6^-$ octahedra take control of the observed behavior. Our results show clear deviation from the pattern found for the isoelectronic $A_x\text{MnF}_{3−x}$ system. The size of the A-site cation is shown to be central in dictating the physical properties and phase transitions in $\text{ACrF}_3$, opening up the possibility of varying the composition to create novel states of matter with tuneable properties.

I. INTRODUCTION

The properties of Jahn-Teller (JT) active materials arise from an intriguing physical interplay between their crystal, orbital and magnetic structures. The hallmark of JT-active systems is orbital frustration (i.e. orbital occupancy degeneracy). This causes structural distortions that break the symmetry and lift the orbital degeneracy.

In crystal field theory, the energy levels of an ion with $d^n$ electronic structure in an octahedral field will split into two sets of energy levels: threefold $t_{2g}$ and twofold $e_g$ states, separated by an octahedral splitting energy $\Delta_o$. When ions with a $d^{|n|}$ electronic configuration such as Mn$^{3+}$ are at the center of a $[BX_n^{-3}]$ octahedron (where $B$ is a cation and $X$ is an anion) there is a further rearrangement of the energy levels, to lower the energy of the highest occupied orbital, creating two tetragonal splitting energies: $\Delta_e$ and $\Delta_t$. This is the JT-effect (See Figure I(a)). In a system transforming from the octahedral point symmetry $O_h$ to JT distorted $D_{4h}$ (Figure I(b)), vibrational modes are introduced corresponding to axial stretching ($Q_\vartheta$) and basal squeezing ($Q_\varepsilon$). The interaction of a doubly degenerate electronic state $E_\vartheta(x^2−y^2, 3z^2−r^2)$ with the two $e_g$ modes ($Q_\vartheta, Q_\varepsilon$) is known as the $E \otimes e$ problem (See Ref. 3). Any point $\rho$ where:

$$\rho = \sqrt{Q_\vartheta^2 + Q_\varepsilon^2} \approx Q_\vartheta$$  \hspace{1cm} (1)

in the $(Q_\vartheta, Q_\varepsilon)$ space will correspond to the ground state (since $Q_\vartheta >> Q_\varepsilon$). The energy gained by having a singly occupied rather than doubly degenerate orbital state is known as the JT stabilization energy, $E_{JT}$, which is proportional to $\rho$.

The energy level diagram (Figure I(b)) shows the point group symmetry ($D_{4h}$) that develops under JT distortion. There are three possible spin allowed transitions from the $^5B_{1g}$ ground state of the $D_{4h}$ point group: $E_1(^5B_{1g} \rightarrow ^5A_{1g})$, $E_2(^5B_{1g} \rightarrow ^5B_{2g})$ and $E_3(^5B_{1g} \rightarrow ^5E_g)$. These spin allowed transitions are defined by the tetragonal splitting parameters and the $E_{JT}$ and are related through the octahedral perturbative scheme 3, 4:

$$E_1 = \Delta_e = 4E_{JT} = K_e Q_\vartheta$$ \hspace{1cm} (2)

$$E_2 = \Delta_{(e\varphi)} \text{ and } E_t = E_3 − E_2 = K_t Q_\vartheta,$$ where $K_e$ and $K_t$ are the electron-ion couplings. It is important to note that all of these phenomena can be explained by the local symmetry of a single octahedron.

Perovskites are crystal structures with the chemical formula $ABX_3$ based on a network of vertex-sharing octahedral units $[B^{n+}X_n^{3−}]$, connected through the B-X-B angle ($\xi^o$), the octahedral tilt or perovskite angle. For an ideal cubic perovskite $\xi^o = 180^o$. In the presence of JT-active ions, the distortions of the octahedra propagate through the crystal lattice, causing $\xi^o$ to move away from $180^o$ and favoring the emergence of long range orbital ordering (OO). This has consequences for the magnetic structure of the JT-active perovskite. The ferromagnetic (FM) interactions occur through antiferromagnetic orbital ordering (AOO), e.g. $|3z^2−r^2|/|3y^2−r^2|$.

X-ray diffraction and optical absorption (OA) spectroscopy experiments under external stimuli (e.g. pressure, temperature, magnetic field) can be used to study...
the interplay between the structure and internal degrees of freedom in JT-compounds. Among the most studied JT systems are the ternary alkali metal/manganese (III) low-dimensional fluoroperovskites $A'_2$MnF$_{3+x}$ (where $A'$ is an alkali/alkali-earth metal and the dimensionality is given by the number of vertex connections between the MnF$_6^{-}$-octahedra, so the $x = 3, 2, 1$ are 0-, 1- and 2-dimensional, respectively). The tetragonal splitting parameters $\Delta_1$ and $\Delta_2$ of $A'_2$MnF$_{3+x}$ increase in a linear manner with dimensionality $[4]$. This manifests itself in the OA spectra as a second set of sharp bands representing the spin-flip transitions. For this family of materials the spin flip bands overlap the spin allowed bands $E_1$, $E_2$ and $E_3$. Valliente et al and Rodriguez et al suggest that oscillating intensities of the spin-flip bands are correlated to the perovskite angle $\xi^\circ$. This angle also controls the symmetry allowed overlap between the orbitals of adjacent ions $[8]$ and thus the magnetic exchange interactions. The oscillating strength of the spin-flip bands also depends on the size of the ion at the $A$-site. The ionic radii of the alkali metals (group 1 of the periodic table) increase significantly with atomic number, providing a good test case for this.

The 2-dimensional fluoride CsMnF$_4$ is a transparent ferromagnet which adopts the tetragonal space group $P4/n$ at room temperature $[6]$. The magnetostructural properties of CsMnF$_4$ at high pressure have been thoroughly studied. High pressure synchrotron XRD (SXRD) experiments showed that CsMnF$_4$ goes through a tetragonal-to-orthorhombic phase transition from $Pa/n \rightarrow Pmnr$ at about $\sim$1.6 GPa $[4]$. Magnetic susceptibility measurements show that this is accompanied by a ferromagnetic to antiferromagnetic (FM-to-AFM) phase transition. OA spectroscopy reveals a high-to-low spin transition at 37.5 GPa in which the three spin-allowed transition bands merge into one $[8]$. The explanation for this is that as the pressure increases $E_{JT}$ is surpassed by the octahedral crystal field splitting energy, $\Delta_O$, forcing Mn$^{3+}$ into the octahedral low spin configuration. This high-to-low spin transition is not observed for the smaller $A'$-site atoms, Na$^+$ and K$^+$ $[7, 8]$.

Chromium (II) fluoroperovskites have been difficult to study owing to the oxygen-sensitive chemistry of Cr$^{2+}$ ions. $KCrF_3$ (which can be prepared by a solid state route) has three temperature dependent polymorphs: cubic ($T > 1000$ K), tetragonal ($T = 1000$ to 250 K) and monoclinic ($T < 250$ K); where the tetragonal to cubic phase transition is suggested to correspond to a metal-insulator transition (MIT) as the OO is removed and orbitals become degenerate $[10, 11]$. There are in addition three magnetic phases (incommensurate-AFM (IC-AFM) between 300 and 79.5 K ($T_N$), commensurate-AFM (CAF) between $T_N$ and 45 K, weak FM and canted AFM below 10 K) $[12]$.

We recently developed a synthesis route for NaCrF$_3$ and were able to explore its structural and magnetic properties for the first time $[13]$. It has a triclinic structure ($P1$) at 300 K with a single canted-AFM magnetic structure below 21 K $[13]$. Measurements of field dependent magnetization - $(M(H))$ below the Néel temperature have revealed the onset of a metamagnetic transition at an applied field of 8 T.

In this paper we study the importance of the $A$-site ion size in the three dimensional perovskite family $A$CrF$_3$ where $A = \text{Na}^+$ (small) or $\text{K}^+$ (large) using temperature and field-dependent OA spectroscopy, supported by crystal structure analysis and DFT calculations. In general we see that as the symmetry of the system is reduced the long range magnetic interactions become weaker and local magnetic structures begin to dominate the behaviour. Our results show that the changes in the spin-flip transitions at low temperature are not correlated to the per-
ovskite angle $\xi$, but rather to the magnetic exchange interactions between neighboring CrF$_6$ octahedra. Merging of the spin-allowed spectral bands $E_2$ and $E_3$ for $A = \text{Na}^+$ shows the emergence at low temperature of an intermediate electronic state where $\Delta_1$ is zero. Furthermore, when an increasing external magnetic field is applied at 2 K, the intensity of the spin allowed bands increases for NaCrF$_3$ but not for KCrF$_3$.

$E_{1/2}$ is larger in NaCrF$_3$ compared to KCrF$_3$, owing to the smaller size of the Na$^+$ ion. Again, we believe this is explained by the local orbital and magnetic ordering rather than the perovskite angle $\xi$. We also present density functional theory (DFT) simulations which calculate the superexchange parameters for the different magnetic orderings possible in each crystal structure, and so, determine the OO of each phase. Finally, we show that the synthesis method we described for NaCrF$_3$ [13] can also be used to produce large volumes of high purity KCrF$_3$.

II. EXPERIMENTAL METHODS

NaCrF$_3$ was prepared according to the method described by Bernal et al. [13] KCrF$_3$ was prepared by a similar method: 0.5 g of chromium (II) acetate hydrate (Cr$_2$(CH$_3$CO$_2$)$_3$(H$_2$O)$_2$; CrOAc) was dissolved in 2 ml deagassed water in a polycarbonate vial sealed with a silicone rubber septum under constant flow of Ar. In a second sealed polycarbonate vial 0.3 g KHF$_2$ was dissolved in 10 mL deagassed water. The KHF$_2$ solution was then injected with a dry syringe into the CrOAc solution. KCrF$_3$ precipitated immediately. Washing with pure methanol rendered both samples air stable. The washed samples were dried under vacuum overnight, and then stored in a glove-box.

Powder X-ray diffraction (XRD) measurements for KCrF$_3$ were performed at the Norwegian Resource Centre for X-ray Diffraction, Scattering and Imaging (RECX) on a Bruker D8 Advance diffractometer in capillary mode with Cu$_{K\alpha}$ radiation selected by a Cu (111) focusing monochromator and a LynxEye XE detector. Synchrotron powder XRD data for NaCrF$_3$ were collected at the Swiss-Norwegian Beam line (SNBL) BM01A of the European Synchrotron (ESRF), Grenoble, France. The setup is described elsewhere [14]. The diffuse reflectance spectra (DRS) were collected on polycrystalline samples of NaCrF$_3$ and KCrF$_3$ with a UV-3600 spectrophotometer (Shimadzu). The low temperature OA experiments were conducted under vacuum in a closed cycle cryostat (Janis Research) with a Fibre-Lite ML-150 halogen lamp (Dolan-Jenner Industries) and USB4000 spectrometer (OceanOptics) in the temperature range 11 - 300 K, and from 1.3 to 2.7 eV.

Field dependent magnetization measurements were carried out on the AC magnetic measurement system -II (ACMS-II) using a vibrating sample magnetometer (VSM) on the Quantum Design (QD) Physical Property measurement system (PPMS). Samples of known weight were loaded into weakly diamagnetic plastic holders and immobilized on brass sample holders at defined height of approximately 25 mm from the bottom of the brass holder. This holder was then loaded into the ACMS-II at the end of a long plastic rod and inserted into the PPMS and cooled down to 2 K. Sample was kept at 2 K for 30 minutes before starting magnetization measurements for thermal homogenization of the sample. The magnetization measurements were carried in sweep mode from 0 to +/- 9 T at a ramp rate of 0.01 T/second and a measurement was taken each second.

Magneto-optic measurements were carried out in a Quantum Design PPMS system. A custom insert was developed using an external DH-2000 Halogen lamp (Mikropack) and USB4000 spectrometer (OceanOptics), both optically connected with the insert using an optical fibre. A long silica rod with the sample powder attached in a gelatin capsule at one end was used to bring light in and out of the vacuum sample chamber and to position the sample appropriately with respect to the PPMS’s superconducting magnets. A LakeShore Cryotronics CER-NOX thermometer was utilized for reading local sample temperature close to the sample.

For temperature dependent measurements, the silica rod mounted sample was inserted into the PPMS cavity and the entire space was evacuated to a soft vacuum at room temperature. The sample and cavity were thermally stabilized before the cool down process was initiated. Cool down from 300 to 2 K was carried out at the rate of 0.5 K/ min and an optical spectrum was taken every 10 seconds. Once the system reached the 2 K temperature set-point a 30 minute delay was given in order for the sample temperature to stabilize, all the while continuously measuring the OA spectra. Magnetic field dependent OA measurements, were made at 2 K and the magnetic field was ramped at 0.01 T/second up to 9 T, continuously measuring OA.

The electronic structures of the NaCrF$_3$ (triclinic- $\overline{I}$) and KCrF$_3$ (monoclinic- $\overline{I}$, tetragonal- $T$, and cubic- $C$) phases were calculated using the Vienna ab initio simulation package (VASP) [15, 16] with the PBE general gradient approximation (GGA) [17]. KCrF$_3$- $C$ was included for comparison, as the highest possible symmetry. The cutoff energy of the plane wave basis set expansion was at least 450 eV. The density of the $k$ point density was determined by a maximum distance between points of 0.25 Å$^{-1}$. Hubbard-corrected GGA+$U$ calculations were performed according to the method described by Meredith et al. [18] with the Coulomb interaction parameter $U$ going up to $U = 9$ eV and the exchange interaction parameter $J_H = 0.88$ for chromium $2^+$. For the calculation of the superexchange parameters, we used the same parameters as in the GGA+$U$ calculations on four possible configurations:

- $F$, (ferromagnetic) in which all the spins are parallel;
- $A$, (antiferromagnetic) in which the intralayer spins
are parallel while the interlayer spins are antiparallel;

- **C**, in which the chains of spins along the z-axis are ferromagnetically coupled, while adjacent chains are aligned antiparallel;

- **G**, in which all nearest neighbor spins are antiparallel.

### A. Structural Analysis of ACrF₃

| TABLE I. Octahedral tilt angles ξ (I) and distortions Δd from XRD for ACrF₃, ξ (I) for NaCrF₃ and ξ (M) for M-KCrF₃ are taken from [12]. ξ (I) is fixed to 180° (ξ ) by symmetry. The calculated octahedral distortions Δd (×10⁻⁴) are given for all phases. |
|-----------------------------------------------|
| Cr | ΔdT | ΔdB | Δdξ |
|-----------------------------------------------|
| 1:  | 65.70 | 56.53 | 78.85 |
| 2:  | - | 69.97 | 55.86 |
| 3:  | - | - | 76.24 |
| 4:  | - | - | 70.73 |

ξ (M)

| Cr1-F3-Cr2 : | 180.0 | l-axial |
|----------------|--------|----------|
| Cr1-F2-Cr2 : | 167.3 | sm-planar |
| Cr1-F1-Cr2 : | 162.3 | sm-planar |

ξ (I)

| Cr1-F5-Cr3 : | 138.797 | l-axial |
|----------------|---------|----------|
| Cr2-F2-Cr1 : | 139.446 | sm-planar |
| Cr2-F1-Cr1 : | 146.589 | sm-planar |
| Cr4-F6-Cr2 : | 140.526 | l-axial |
| Cr4-F4-Cr3 : | 142.357 | sm-planar |
| Cr4-F3-Cr3 : | 141.683 | sm-planar |

To analyze the ACrF₃ systems, we use a pseudocubic lattice (PL) derived from the unit cell of the high T cubic KCrF₃ phase. Its vertices lie at the centers of 8 neighboring CrF₆⁻ octahedra, and its lattice parameters are a_p ≈ b_p ≈ c_p. The JT distorted octahedra have short (s, ca. 1.9 Å), medium (m, ca. 2.0 Å) and long (l, ca. 2.3 Å) Cr-F bonds, the relative orientation of which depends on the orbital ordering. The s, m and l bonds can be used to describe the orientations of isolated CrF₆⁻ octahedra. For example, the tilt angle ξ along the l-bonds can be described as l-axial, and if a bond lies within the plane formed by the s and m bonds, then, it is described as the sm-plane of the octahedra. The octahedral distortion parameter Δd used to quantify the distortion (ref Shannon) is also calculated from the s, m and l Cr-F bond lengths around the octahedron:

$$\Delta d = 1/6 \sum_{i=1}^{i=6} \frac{|l_i - l_{av}|}{l_{av}}$$  (3)

Where l_i for i = 1-6 is the 6 Cr-F bond lengths, (2 each of s, m and l) and l_{av} is the average of s, m and l [12].

In general we can describe all of the structures as having layers in the s, l plane where neighboring octahedra are rotated 90° about the m-axis to create a motif of alternating s and l Cr-F bonds. These layers are linked by m Cr-F bonds. The PL is aligned relative to the tetragonal (T), monoclinic (M) and triclinic (I) crystallographic unit cells such that the network of alternating s and l bonds lies in the a_p, b_p plane and the linking m bonds are aligned along c_p (see Figure 2 (c)). Figure 2 (c) shows the relationship of the PL to the (T), (M) and (I) unit cells of the ACrF₃ family. The tilts (ξ) of the octahedra relative to the edges of the ideal PL increase as the symmetry is lowered. The layers of alternating s and l bonds in the a_p, b_p plane are stacked with adjacent layers mirrored in the a_p, c_p plane. This creates an A, B, A, B... sequence. At the orbital level this means that the OO consists of [d₃ₓ²₋ₙ₋₂]/[d₃ᵧ²₋ₙ₋₂] AOO layers stacked along the c_p-axis.

In an ideal cubic perovskite all ξ = 180° (ξ ). The higher the number of ξ vertex-angles in a system, the stronger the magnetic exchange interactions due to proper orbital overlap. To the ideal system described by the PL, we applied the perturbative model [3, 4] to describe the structural parameters related to the JT-distortions from the XRD-patterns. Inspection of the powder XRD pattern (Figure 1) confirmed that our syntheses yielded single phase polycrystalline T-KCrF₃ (space group I4/mcm) and I-NaCrF₃ (space group P1) at room temperature. Octahedral distortion parameters Δd for the three ACrF₃ phases, and perovskite tilt angles ξ for M-KCrF₃ and 2-NaCrF₃ are given in Table I [11].

Δd for T-KCrF₃ is 65.7×10⁻⁴. It adopts the zero-tilt configuration described by Glazer notation aₙaₙ₋₁ aₙ [20] so that all perovskite angles are ξ. The ξ angles within the AOO layers create strong in-plane FM interactions propagating along the a_p and b_p axes. The magnetic superexchange parameters within the AOO-planes display FM character through σ interactions between half-filled [d₃ₓ²₋ₙ₋₂] and empty [d₃ᵧ²₋ₙ₋₂] Cr⁺² orbitals bridged by |pₙ⟩ orbitals of F⁻ ions. The orthogonal ξ perovskite angle along the c_p-axis (absent in the low dimensional A₄⁺MnF₃₊ₓ systems) leads to a ferrodistortive OO (FOO) with an AFM coupling between adjacent over-
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FIG. 2. (a) Observed (black dots) and calculated (red line) X-ray powder diffraction (XRD) for T-KCrF₃ (λ = 1.5405 Å) at 258 K (a = 6.051317, c = 8.024635 Å). Agreement factors of the Rietveld refinement: \( R_{wp} = 16.09476\% \); \( R_{exp} = 5.3272\% \). The solid blue line shows the difference between the observed and calculated intensities, and the ticks indicate the allowed Bragg reflection positions. The inset shows the high angle fit. (b) Final observed Synchrotron XRD profiles (λ = 0.709 Å of NaCrF₃ at 298 K (a = 5.5100, b = 5.69190, and c = 8.18860 Å). The agreement of the Rietveld refinement: \( R_{wp} = 3.321219\% \) and \( R_{exp} = 0.014351\% \). The very low \( R_{wp} \) value is due to the use of an area detector (ref). (c) Schematic representations of, from left to right: the pseudocubic unit cell with \( a_p = b_p = c_p \) (PL), the PL embedded within the tetragonal (T), monoclinic (M) and triclinic (I) unit cells of ACrF₃. The OO motif of the \(|d_{z^2}\rangle \) (i = x, y, z) orbitals is shown.

M-KCrF₃ (space group \( I112/m \)) appears on cooling to \( T = 250 \) K \([10]\). Two crystallographically non-equivalent Cr sites (Cr1, Cr2) are generated in this form with \( \Delta d \) values of 56.53 \times 10^{-4} \) and 69.97 \times 10^{-4} \). Within the \( a_p, b_p \) and \( c_p \) planes there are tilts corresponding to Glazer notation \( a^{-}b^{-}c'^{0} \), in which, the Cr1-F1-Cr2 and Cr1-F2-Cr2 angles are 162 and 167°, respectively. The loss of symmetry leaves a single \( \xi^\pi \) vertex angle along the \( c_p \)-axis where proper orbital overlap is preserved for FM interactions to propagate. The orbital overlap for AFM interactions also becomes weaker which can be interpreted as weak FM interactions since the \(|d_{x^2-y^2}\rangle - |p_x\rangle - |y^2-z^2\rangle \) relationship is weakened.

NaCrF₃ crystallizes in a NaCuF₃ type structure with space group \( P1 \) \([21]\). Four nonequivalent crystallographic sites (i.e. Cr1, Cr2, Cr3 and Cr4) are present for Cr²⁺ in NaCrF₃ \([13]\), with \( \Delta d \) and \( \xi^\pi \) values give in table 1. The \( \Delta d \) values for NaCrF₃ are greater than those of the KCrF₃ phases, indicating greater JT distortion. The CrF₆⁻ units are tilted in all directions, adopting the Glazer tilt \( a^{-}b^{-}c^{-} \). This means that NaCrF₃ has no \( \xi^\pi \) angles, which is reflected in a significant reduction in the strength of the overall magnetic interactions. Consequently, the AOO adopts a canted motif where \(|d_{z^2}\rangle \)
orbitals on Cr1 and Cr4 tilt about the b\textsubscript{p}-axis and Cr2 and Cr3 are tilted about the a\textsubscript{p}-axis.

B. Electronic Structure of ACrF\textsubscript{3}

The calculated octahedral and tetragonal splitting parameters for the ACrF\textsubscript{3} phases, as a function of the electron-electron correlation parameter U, are presented in Figure 4. For C-KCrF\textsubscript{3} there is no JT distortion and the octahedral splitting parameter \( \Delta O \) is present at all levels of correlations, preserving the orbital degeneracy of the \( e_g \) orbitals.

This invariance under \( U \) suggests that electron-electron correlations lead to neither OO nor MIT in C-KCrF\textsubscript{3} within the framework of our calculations. For T- and M-KCrF\textsubscript{3} phases, the emergence of the tetragonal splitting parameter \( \Delta a \) occurs simultaneously at \( U=\pm 1.7 \) eV. This may suggest that the OO and MIT in both T- and M-KCrF\textsubscript{3} phases emerges as consequence of strong electron correlations. However, the calculations were performed on the already distorted low symmetry KCrF\textsubscript{3} which excludes electron-electron correlations as the source of the OO. In other words, structural distortion is necessary for OO to occur. Replacing K\textsuperscript{+} with Na\textsuperscript{+} in ACrF\textsubscript{3} increases \( E_{JT} = \Delta a/4 \) even at \( U=0 \) and from this point its increase with \( U \) has a similar curvature to T- and M-KCrF\textsubscript{3}. Our calculations support the structural results where \( E_{JT} \), which is related to \( Q_0 \) (Equation 2), is larger for NaCrF\textsubscript{3} than KCrF\textsubscript{3}. At \( U=0 \) NaCrF\textsubscript{3} preserves the orbital degeneracy of the \( e_g \) orbitals showing that the phonon-electron interactions that characterise the JT-effect are the driving force for OO.

We calculated the ground-state energies of the low-symmetry ACrF\textsubscript{3} phases with four magnetic orderings A, F, C, G and then the magnetic exchange parameters \( J_B \) (basal) within the \( a_pb_p \)-plane of the pseudocubic unit cell, and \( J_A \) (axial) along the \( c_p \)-axis according to: \( J_A = [E(F) - E(G) - E(A) + E(C)]/4S^2 \) and \( J_B = [E(F) - E(G) + E(A) - E(C)]/8S^2 \). Figure 5 shows the energies of the superexchange parameters as function of \( U \) for the tetragonal, monoclinic and triclinic phases of ACrF\textsubscript{3}. For T-KCrF\textsubscript{3} the calculated axial superexchange parameter is \( J_A(T) > 0 \) for \( U < 1.9 \), and become weakly negative for \( U \geq 2 \) suggesting weak AFM interactions between AOO layers. The basal superexchange \( J_B(T) \) decreases at all levels of correlations but is
always positive with $J_B(T) > J_A(T)$. This picture agrees with the one described in the structural section, in which $T$-KCrF$_3$ contains only $\xi^a$ vertex angles, both within its AOO $a_p$b$_p$-plane (with strong in-plane FM interactions) and connecting the AOO layers. In $M$-KCrF$_3$, the loss of symmetry leaves a single $\xi^a$ along the $c_p$-axis. The calculated superexchange parameters of $M$-KCrF$_3$ confirm that $J_A(M), J_B(M) > 0$ with $J_A(M) > J_B(M)$, the opposite of the tetragonal form. Again, this agrees with the structural analysis, describing a single $\xi^a$ in the $c_p$-axis direction, giving strong FM interactions propagated along the $c_p$-axis.

In NaCrF$_3$, the smaller Na$^+$ ion on the $A$-site induces additional octahedral tilts in all directions with no $\xi^a$ vertex angles, accompanied with larger octahedral distortions (Table II). This further reduces strength of the magnetic interactions as the orbital overlap decreases. The canted AOO propagates within the $a_p$c$_p$-plane. NaCrF$_3$ has $J_A(I) \sim J_B(I) > 0$ with increasing $U$. Comparing to the higher symmetry systems found in KCrF$_3$, $J_A(B)(M) > J_A(B)(I)$ indicates that the magnetic interactions are weakest at the lowest symmetry. We observe that $J_A(T) > J_{A,B}(M) > J_{A,B}(I)$ for $U < 4$ but for $U \geq 4 J_A(T)$ and $J_A(M)$ converge. Again this is consistent with the structural analysis, where increasing distortion reduces orbital overlap.

C. Temperature and magnetic field dependent OA Spectroscopy

Figure 6 shows the OA-spectra at 300 K for KCrF$_3$ and NaCrF$_3$, respectively. The spectra are very similar in the location of the observed bands. For ACrF$_3$ there is no overlap between the spin allowed and the spin forbidden transitions, in contrast to the $A_x$MnF$_{3+x}$ family. The quintet-quintet or spin-allowed ($E_{SA}$) transitions (Figure 6 (b) and (c)) lie between 1.3 and 2 eV. They are labeled here as $E_{SA}$ corresponding to $E_1(^5B_{1g} \rightarrow ^5A_{1g})$, $E_2(^5B_{1g} \rightarrow ^5B_{2g})$ and $E_3(^5B_{1g} \rightarrow ^5E_{2g})$. The region between 2 and 2.6 eV contains the quintet-triplet, or spin-flip ($E_{sf}$) transitions: $E_4(^5B_{1g} \rightarrow ^3B_{1g})$ and

![OA spectra image](image)

**FIG. 6.** OA spectra of (a) KCrF$_3$ and (b) NaCrF$_3$ at 300 and 2 K corresponding to the $E_{SA}$ region with their respective convolution fits.

| $E_{300K}$ | $E_1$ | $E_2$ | $E_3$ | $\Delta_1$ | $E_{JT}$ |
|-------------|-------|-------|-------|------------|---------|
| Cr          |       |       |       |            |         |
| NaCrF$_3$   | 1.42  | 1.65  | 1.82  | 0.20       | 0.355   |
| KCrF$_3$    | 1.40  | 1.66  | 1.78  | 0.12       | 0.350   |

| $E_{2K}$ | $E_1$ | $E_2$ | $E_3$ | $\Delta_1$ | $E_{JT}$ |
|----------|-------|-------|-------|------------|---------|
| Cr       |       |       |       |            |         |
| NaCrF$_3$| 1.42  | 1.65  | 1.82  | 0.20       | 0.355   |

**TABLE II.** Calculated JT vibrational modes and fitted spin-allowed band positions in the OA spectra of ACrF$_3$. The normal modes are calculated from the bond distances in the octahedral units in Å according to Equations II. Fitted positions of the $E_{300K}$ bands in eV at 300 K. Tetragonal parameters $E_3 = \Delta_e$ and $\Delta_g = E_3 - E_2$ along with the JT-stabilization energy $E_{JT}$ given in eV.

![Table image](image)
Thus the functions, \( \alpha_t \) and \( \alpha_s \), in the PPMS between 300 and 2 K and fitted the vertex angles. The Ne\'el temperature of NaCrF\(_3\) is 1.40 K and NaCrF\(_3\) and ZFC magnetic susceptibility \( \chi \) in the interval 2 to 300 K. The two vertical dashed lines at \( T_N = 21.5 K \) (brown) and \( T_1 = 48.6 K \) (red) indicate the Ne\'el temperature of NaCrF\(_3\) and the IC-to-AFM transition in KCrF\(_3\), respectively. (b) Close-up of the \( E_{\text{SF}} \) and \( \chi \) in the range of 4-60 K. (c) Polar angle \( \vartheta \) plotted with \( E_{\text{SF}} \) intensity for NaCrF\(_3\). The vertical blue dashed line at 9 K marks the reduction of oscillating strength and the final convergence of the polar angle for Cr1 and Cr3 Ref [13].

The fitted positions and oscillating intensities of the spin allowed bands at 300 K and 2 K are given in Table II along with the \( \Delta_t \) and \( E_{\text{JT}} \) values. The \( E_{\text{SA}} \) transitions of KCrF\(_3\) are \( E_1 \) = 1.42, \( E_2 \) = 1.65 and \( E_3 \) = 1.82 eV at 300 K. At 2 K the positions of \( E_1 \), \( E_2 \) and \( E_3 \) remain almost the same but their intensities decrease. The JT-stabilization energy \( E_{\text{JT}} \) (Equation 2) for KCrF\(_3\) is 0.355 eV at 300 K and remains nearly unchanged down to 2 K. The second tetragonal parameter, \( \Delta_r \), is 0.20 eV at 300 K and also remains unchanged down to 2 K. The \( E_{\text{SA}} \) energy transitions of NaCrF\(_3\) are \( E_1 \) = 1.40, \( E_2 \) = 1.66, and \( E_3 \) = 1.785 eV at 300 K. At 2 K \( E_1 \) and \( E_2 \) shift to higher energies by 50 meV, and 448 meV, respectively. This means that reduction of ion size at A-site induces an increment in \( E_{\text{JT}} \) of 12.5 meV at 2 K which in turn is 7.5 meV higher than \( E_{\text{JT}} \) of KCrF\(_3\). The fit at 2 K shows that there is a total merging of the \( E_2 \) and \( E_3 \) bands as shown in Figure (b). It follows that the tetragonal parameter \( \Delta_t \) of NaCrF\(_3\) disappears and that \( \Delta_r/\Delta_t \to \infty \) as \( \Delta_r \to 0 \). This means that with decreasing temperature contributions to \( E_{\text{JT}} \) from \( \sigma \) bonding become stronger in NaCrF\(_3\) than KCrF\(_3\). This effect is due to the reduced symmetry caused by the ion size reduction at the A-site. The vibrational mode frequencies \( Q_\vartheta \) and \( Q_\varepsilon \) for ACrF\(_3\) are calculated from the bond lengths by:

\[
Q_\vartheta = (1/\sqrt{3})(2l - m - s), \quad Q_\varepsilon = m - s \quad (4)
\]

The values are given in Table III. For all three phases \( Q_\vartheta > Q_\varepsilon \) which suggests that orbitals with \( |d_{3z^2-r^2}\rangle \) symmetries are being occupied. The normal tetragonal mode \( Q_\vartheta \) (i.e. stretching of octahedral unit) increases on average with decreasing symmetry. Since \( E_{\text{JT}} \sim Q_\vartheta \sim \rho \) (See Equation 1) we see that \( Q_\vartheta(\mathcal{I}) > Q_\vartheta(\mathcal{M}) > Q_\vartheta(\mathcal{T}) \) in Table III thus the \( E_{\text{JT}} \) for NaCrF\(_3\) is larger than in KCrF\(_3\) indicating that the reduction of the A-ion size reinforces the JT-phenomenon.

The intensities of the \( E_{\text{SF}} \) bands were taken from the integrated intensities of the two peaks for all temperatures. Figure (a) shows the fitted \( E_{\text{SF}} \) intensities in both phases as a function of temperature, superimposed on the zero-field cooling (ZFC) magnetic susceptibility, \( \chi \), of both phases at an applied magnetic field of 1 T. Figure (b) shows a close-up below 60 K to clarify the behavior. The temperature (\( T_1 \)) in KCrF\(_3\) corresponding to the IC-AFM to C-AFM transition (Ref. [12]) and the Ne\'el temperature (\( T_N \)) of NaCrF\(_3\) are 48.6 K and 21.5 K respectively, with both having magnetic moments \( \mu_{\text{eff}} \sim 4.47 \mu_B \) following the spin-only configuration \( S = 2 \) for Cr\(_{2+}\). The two samples obey the Curie-Weiss (CW) in different temperature ranges: 300-100 K for KCrF\(_3\) and 300-24 K for NaCrF\(_3\). The Curie temperatures \( \theta \) of KCrF\(_3\) and NaCrF\(_3\) are 1.7 and -4 K respectively (Refs. [12, 12]).

We observe a direct magneto optic correlation between the normalized integrated intensities \( E_{\text{SF}} \) of KCrF\(_3\) and its magnetic ordering as the intensities of \( E_{\text{SF}} \) start de-
increasing smoothly at $T_1$. This is not observed for the case of NaCrF$_3$ where the $E_{SF}$ intensities decrease abruptly between 9 and 8 K. The disappearance of the $E_{SF}$ bands is likely to lead to a thermochromic effect, but we have not as yet been able to observe this. According to our recent neutron powder diffraction (NPD) studies on NaCrF$_3$ (Ref. [13]) NaCrF$_3$ adopts a canted A-type AFM ordering. The refinements were performed using polar coordinates with polar and azimuthal degrees of freedom ($\theta, \varphi$). The polar angle $\varphi^o$ measures the out-of-plane spin canting from the $a_p$-$c_p$-planes, and the azimuthal angle $\theta^o$ the spin canting within the $a_p$-$c_p$-planes.

Figure 8 (c) shows the comparison of the $E_{SF}$ intensities of NaCrF$_3$ below 9 K against the temperature dependent polar angle $\varphi^o$ from the neutron powder diffraction (NPD) data (Ref. [13]). We observe that below 9 K, as the $E_{SF}$ bands disappear, the polar angles of Cr$_1$ and Cr$_3$, $\varphi^o_1$ and $\varphi^o_3$ approach the same value (Note: The $\varphi^o$ components of the magnetic moments of the Cr$^{2+}$ ions were constrained in the NPD refinements for Cr$_2$ and Cr$_3$ as follows: $\varphi^o_2 = \varphi^o_1 + 180$ and $\varphi^o_4 = \varphi^o_3 + 180$, so only $\varphi^o_1$ and $\varphi^o_3$ are quoted here).

After the temperature reached 2 K, we performed field dependent OA experiments for both KCrF$_3$ and NaCrF$_3$ to explore possible correlations with the field dependent experiments $M(H)$ in Ref. [13] which metamagnetic transitions were observed for NaCrF$_3$. Quick inspection of the field dependent magnetic measurements in Figure 8 (a) shows that the plot for KCrF$_3$ is linear while that of NaCrF$_3$ is not. This agrees with our previous results [13]. This indicates the presence of metamagnetism in NaCrF$_3$, but not KCrF$_3$. Figure 8 (b) shows the integrated intensities of the $E_{SA}$ bands of KCrF$_3$ and NaCrF$_3$ as a function of magnetic field in steps of 0.5 T in the field region between 0 - 9 T at 2 K. The integrated normalized oscillating strength of the $E_{SA}$ transitions in NaCrF$_3$ increases with magnetic field, while for KCrF$_3$, it remains constant.

D. Discussion

The JT-active $ACrF_3$ systems, where, $A = K^+, Na^+$ display interesting magneto-optic and structural phenomena under external stimuli. XRD reveals that with decreasing ion size at the $A$-site, $E_{JT}$ increases as $Q_{2I}(T) > Q_{2I}(T) > Q_{2I}(M)$. Calculations of splitting parameters for all phases of $ACrF_3$ show that: (1) the electron-ion JT $E \equiv e$ coupling is essential for the OO to occur. (2) A MIT was observed for $T$ and $M$ for $U > 1.5$ eV. This indicates that for OO to occur, JT-distortions must already be in place. This is confirmed with the substitution $K^+ \rightarrow Na^+$. (3) At zero electron-electron correlation the tetragonal splitting parameter $\Delta_e$ is zero (ie., $\Delta_e \neq 0$ for all $U$). Since the stabilization energy $E_{JT} = \Delta_e/4$, therefore a direct correlation between the results of the structural analysis and the calculations supports that $E_{JT}(T) > E_{JT}(T, M)$.

As symmetry is lowered and the number of $\xi^o$ decreases, so does the strength of the magnetic interactions. This establishes a magneto-structural correlation between the $\xi^o$ vertex angles and the magnetic superexchange parameters. The calculated super exchange parameters $J_A$ and $J_B$ show that by decreasing the lattice symmetry (and thereby the number of $\xi^o$ vertex angles) the magnetic interactions reduce in strength regardless of $U$. Thanks to the fact that the $E_{SA}$ and $E_{SF}$ bands in the OA spectra of $ACrF_3$ do not overlap, we can address the effect of external stimuli on the two types of transition independently.

Temperature dependent OA-measurements show that for KCrF$_3$ the $E_{SA}$ energies are not effected by temperature in the range studied. For NaCrF$_3$ the $E_{SA}$ transitions are shifted to higher energies with decreasing temperature with $E_2$ and $E_3$ actually merging at 2 K. This means that $\Delta_3$ tends to becomes zero, which indicates that electron-ion couplings arising from $\pi$-couplings in NaCrF$_3$ are nearly absent and $\Delta_e/\Delta_3 \rightarrow \infty$.

The $E_1$ band in NaCrF$_3$ shows a slight blue-shifting at 2 K, which can be interpreted as an increase in $E_{JT}$ with respect to KCrF$_3$, again showing that reducing the size of the ion at the $A$-site increases $E_{JT}$. The $\Delta_e$ values ob-
tained from the OA-measurements of ACrF₃ lie between ∆ₐ values of A₄⁺MnF₃ and A₅⁺MnF₅ [4], ∆ₑ, and thus E₉₄ for ACrF₃ do not follow the linear relation between ∆ₑ and dimensionality proposed for the A₄⁺MnF₃₊ₓ family.

The increase in E₉₄ band intensity with increasing magnetic field for NaCrF₃ at 2 K is not observed for KCrF₃ or other related Cr₂⁺ fluorides, e.g. Rb₂CrCl₄ in which the E₉₄ transitions decline in intensity with increasing magnetic field [22, 23]. The increase could be related to the orbital structure and spin ordering correlations described in the Kugel-Khomskii Hamiltonian [21]. However, at this point we cannot establish a direct correlation between the two effects and further theoretical and experimental studies are necessary for proper interpretation of these results.

No significant changes in the E₉₄ intensities are observed in the OA-spectra of KCrF₃ at the T-to-M transition. Based on the A₄⁺MnF₃₊ₓ family, in which the E₉₄ transitions are related to ξ and thus to the magnetic superexchange interactions Jₐ(B), we expected the intensities to decrease as the number of ξπ is reduced. Instead of changing at the crystallographic phase transition, the E₉₄ intensities of KCrF₃ drop at the IC-to C-AFM transition at T₁ = 48.5 K. In NaCrF₃ the E₉₄ transition intensities decrease abruptly below 9 K instead of at the Neél temperature of 21.5 K as might be expected. The magnetic susceptibility measurements of NaCrF₃ show a weak ferromagnetic upswing between 9 and 8 K which coincides with the fall in the E₉₄ intensities. The polar components of the spins ϕ in NaCrF₃ established by the NPD measurements describe the component of the spins departing from the canted AO layers. The ϕ converge below 9 K in a similar pattern to the E₉₄ intensities. The reduction of the E₉₄ at T₁ in KCrF₃ and at 9 K in NaCrF₃ indicates that the intensity of E₉₄ is controlled by the magnetic structure and not the crystal structure, a direct magneto-optical correlation. No magneto-structural correlations were observed at standard pressure in either temperature or field dependent OA experiments.

III. CONCLUSIONS

The magneto-optical and structural properties of fluoro-perovskites ACrF₃ where A = Na⁺, K⁺ display trends that contrast strongly with those reported for the A₄⁺MnF₃₊ₓ family.

Analysis of the E₉₄ bands in the OA spectra (supported by DFT calculations and XRD characterization) shows that having the smaller Na⁺ ion at the A-site increases the JT- stabilization energy, EJT. Field-dependent OA measurements of the E₉₄ in NaCrF₃ show magneto-optical correlations absent in KCrF₃ and other related structures. The collapse of the E₉₄ intensities in ACrF₃ below 48.6 K is directly linked to the local magnetic interactions and not the crystal structure- the more the order of the structure is reduced, the more significant the local interactions based on the magnetic properties of individual CrF₆⁻ octahedra become. In conclusion, the ion size at the A-site controls the physical properties of the ACrF₃ fluoroperovskites. This, combined with the reliable synthesis routes we have developed for this family of materials, opens up the possibility of discovering novel states of matter by manipulating the A-site.

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