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Spin transition in Co^{3+} by optical absorption and time-resolved spectroscopy under pressure: an appraisal of the different spin states

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This work investigates the electronic structure of CoF_3 by optical absorption and its relationship with the ground-state spin and the Jahn–Teller (JT) effect exhibited by $\text{Co}^{3+}(\text{d}^6)$ in octahedral coordination (CoF_6)³⁻. The results are compared with other Co^{3+} fluorides and oxides, where Co^{3+} is high spin (HS) and low spin (LS), respectively. In CoF_3 we detect an absorption band with a doublet structure at 1.89 eV (657 nm) and 1.45 eV (855 nm) at 2.5 GPa, which is associated with the $T \otimes e$ JT effect on the 5T_2 HS ground state. Absorption measurements under pressure have been carried out around the HS–LS (${}^5T_2 \leftrightarrow {}^1A_1$) spin crossover transition in the 0–20 GPa range. We show that the JT effect is stable in a wide pressure range. No sign of intermediate spin (${}^3T_{1,2}$ states) is observed in the explored pressure range.

Keywords: Co^{3+} ; CoF_3 ; spin crossover; intermediate spin; Jahn–Teller

1. Introduction

There is some controversy about the existence of intermediate spin (IS; $S=1$) in Co^{3+} ions ($3d^6$) around the $S = 0$ (1A_1) to $S = 2$ (5T_2) spin crossover transition (SCO). The observation of magnetic moments with values of $\mu_{\text{eff}} > 0$ for $T > 0$ K that increase with temperature in Co^{3+} oxides [1] has been explained in terms of either a mix of IS and low spin (LS) states around SCO or high spin (HS) and LS states, which actually corresponds to $S = 1$ or $S = 2$ and $S = 0$ spin states in thermal equilibrium, respectively [1–3]. Insulating oxides and fluorides are attractive systems for elucidating such a controversy since they provide a crystal-field strength, Δ_{CF} , for Co^{3+} at, or nearly below, the SCO (${}^5T_2 \leftrightarrow {}^1A_1$): $\Delta_{\text{CF}} = 2.1$ [4] and 1.7 eV [5], respectively. According to the Tanabe–Sugano diagram for Co^{3+} ($3d^6$), the SCO crystal field is 20 times the Racah parameter B , which is $\Delta_{\text{SCO}} = 1.9$ eV for $B = 0.095$ eV derived from the optical spectra [4,6]. Magnetic measurements and X-ray emission spectroscopy (XES) performed on CoF_3 and LaCoO_3 clearly indicate that the low temperature ground state corresponds to HS ($S = 2$) [7–9] and LS ($S = 0$) [9–10], respectively. XES was employed to explore the increase of spin with

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temperature in LaCoO_3 as a probe for IS [9]. However, the proof of IS on the basis of an $S = 1$ state in Boltzmann equilibrium with a $S = 0$ state, as deduced from magnetic measurements [10], is doubtful since the magnetic data can also be interpreted in terms of the ${}^5\text{T}_2$ HS state split by the spin-orbit and trigonal crystal field in LaCoO_3 [11]. High-resolution X-ray diffraction experiments were performed in order to prove the involvement of the IS state in the magnetic properties of LaCoO_3 by measuring the distortion of the CoO_6 octahedron due to the $\text{E} \otimes \text{e}$ Jahn–Teller (JT) effect associated with IS (${}^3\text{T}$) [2]. It is shown that CoO_6 exhibits a slight distortion with three different Co–O bond distances: 1.87, 1.93 and 1.99 Å at $T = 295$ K. The distortion parameter of the octahedron due to the JT effect, defined as $\rho = [Q_\theta^2 + Q_\epsilon^2]^{1/2}$ [12], is $\rho = 0.12$ Å. But such a distortion seems to be very small for a $\text{E} \otimes \text{e}$ JT effect if we take into account well known distortions in $\text{E} \otimes \text{e}$ systems such as LaMnO_3 with an averaged four short Mn–O distances of 1.94 Å and two long Mn–O of 2.18 Å ($\rho \approx Q_\theta = 0.24$ Å) [13] and the big JT effect ($\text{E} \otimes \text{e}$) required to stabilize the IS state ($E_{\text{JT}} \approx \Delta_e/4 \approx 0.6$ eV/ Co^{3+}) [14].

In this work we investigate the electronic structure of Co^{3+} -doped LaAlO_3 and CoF_3 by optical spectroscopy under pressure. The aim is to obtain the crystal-field spectra and particularly the orbital splitting related to the JT distortion for different electronic ground states: weakly $\text{T} \otimes \text{e}$ for HS (${}^5\text{T}_2$) and strongly $\text{E} \otimes \text{e}$ (plus $\text{T} \otimes \text{e}$) for the supposedly low-lying first-excited state IS (${}^3\text{T}_{1,2}$).

2. Experimental

CoF_3 was obtained from Sigma–Aldrich and Co-doped LaAlO_3 crystals were synthesized following the procedures indicated elsewhere [15]. Due to the high reactivity of CoF_3 in air, silicone oil and paraffin, special care was paid for handling and loading the diamond anvil cell (DAC) in Argon atmosphere using a glove box.

The optical spectra of Co-doped LaAlO_3 were obtained in a Cary 6000i spectrophotometer operating directly in reflectance mode and in absorption mode, using KBr-diluted sample pellets (12.5 mol%) in the latter case. The absorption spectra of CoF_3 were directly obtained by compacting CoF_3 powders with no hydrostatic medium in the DAC together with several ruby chips homogeneously distributed in the gasket hole. This procedure guarantees a full absorption measurement from the sample. The experimental setup is a homemade single beam microspectrometer (Nikon microscope with an output optical fibre attached to a HR-320 Jobin–Yvon monochromator), using a SR440 lock-in amplifier and suitable Hamamatsu InGaAs and R928 photomultiplier detectors for synchronous detection.

3. Results and discussion

Figure 1 shows the three possible spin states for Co^{3+} and the corresponding one-electron level diagram taking into account the strength of the JT effect associated with each state. For illustration purposes, Figure 1 also shows the absorption spectra corresponding to trivalent transition-metal ions exhibiting JT distortions of $\text{T} \otimes \text{e}$ ($\text{Cs}_2\text{NaCoF}_6$) and $\text{E} \otimes \text{e}$ (Na_2MnF_5), as well as others having regular octahedron coordination (Rb_2KCrF_6). The observed absorption bands correspond to electronic transitions between the octahedral e_g and t_{2g} orbitals split in a different way depending on the strength of the JT distortion. For a strong $\text{E} \otimes \text{e}$ JT effect, the spectrum of Na_2MnF_5 consists of three bands located in the visible range at 1.55, 2.23 and 2.62 eV, consistently with a JT distortion of $Q_\theta = 0.29$ Å [12]. They correspond to spin-allowed electronic transitions between one-electron orbitals e_g and t_{2g} , split both by the octahedral crystal field and the low symmetry distortion due to

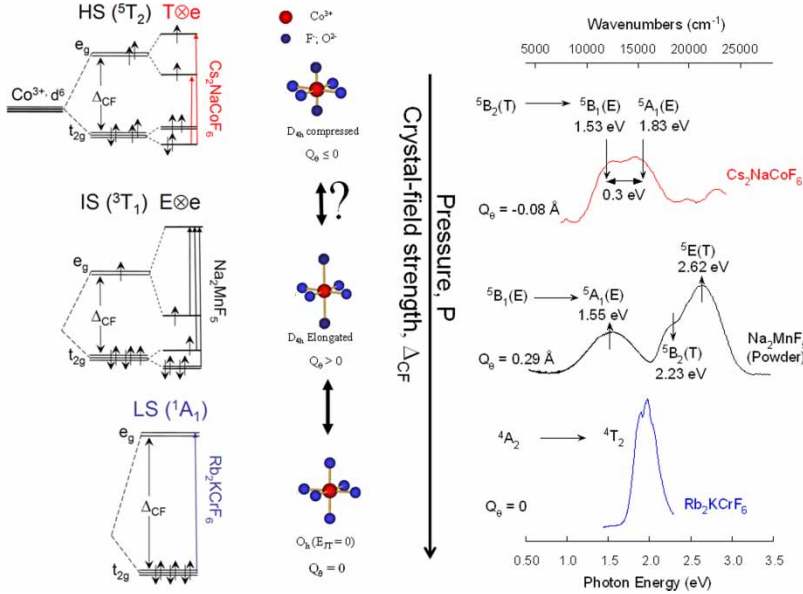


Figure 1. (Left) Schematic representation of the energy for the three possible spin states of six-coordinated Co³⁺. The one-electron level diagram includes the JT effect for each state. Arrows indicate the transitions corresponding to the spectra on the right side. (Right) Absorption spectra of Co³⁺ taken from [5], Mn³⁺ [12] and Cr³⁺ [16] exhibiting JT distortions of T ⊗ e (Cs₂NaCoF₆) and E ⊗ e (Na₂MnF₅), and regular octahedron coordination (Rb₂KCrF₆).

the JT effect [12]. The JT stabilization energy is given by 1/4 of the e_g splitting: $E_{JT} = 1/4\Delta_e = 0.39 \text{ eV/Mn}^{3+}$ for $\Delta_e = 1.55 \text{ eV}$ in Na₂MnF₅. The corresponding t_{2g} splitting, $\Delta_t = 0.39 \text{ eV}$, can be obtained from the two bands at higher energy and corresponds to approximately 1/4Δ_e. The situation for Co³⁺ (T ⊗ e) is different. The one-electron diagram is basically the same for Co³⁺ and Mn³⁺ but the distortion is smaller for Co³⁺ due to the weaker T ⊗ e coupling with respect to E ⊗ e. The first transition energy for d⁶ corresponds to Δ_t and the difference between the other two transitions, which are those usually observed in VIS-NIR, gives Δ_e. The two bands observed in HS Co³⁺ fluorides, actually correspond to the t_{2g} → e_g transition split by the JT effect (T ⊗ e) and eventually by the crystal anisotropy [5]. It is worth noting that in an eventual IS ground state the optical spectrum of Co³⁺ (band structure and transition energies) would be similar to the spectrum of Mn³⁺ in HS for a similar low-symmetry distortion associated with E ⊗ e. In fact, the splitting of the absorption band for Cs₂NaCoF₆ and CsCoF₄ directly gives Δ_e = 0.3 and 1.0 eV, respectively (Figure 2). The latter splitting is smaller than Δ_e for Mn³⁺ in Na₂MnF₅ and NaMnF₄ [12] thus indicating that distortions are significantly shorter in Co³⁺, as corresponds to the weakly T ⊗ e JT effect [5,12]. Q_θ (and ρ) values in Cs₂NaCoF₆, CsCoF₄ [5] and Na₂MnF₅, NaMnF₄ [12] are 0.08, 0.18, 0.29 and 0.38 Å, respectively. These distortions are in agreement with their corresponding Δ_e values as they are obtained by the relationship that links the JT distortion, $\rho = [Q_\theta^2 + Q_\epsilon^2]^{1/2}$, and the tetragonal splitting Δ_e, as:

$$\Delta_e = 5.1\rho, \quad (1)$$

where Δ_e is given in eV and ρ in Å; ρ being positive or negative for elongated or compressed distortions, respectively [12]. Such a correlation applies also for Mn³⁺ in epidote (ρ = 0.28 Å) [4], and is obeyed for Co³⁺ fluorides as well (Figure 1) [5]. It must be noted that in CrF₆³⁻ the first absorption band does not show any structure related to the JT effect as it corresponds to an orbital singlet ground state (⁴A₂) with ρ = 0 Å, and Δ_{CF} = 1.9 eV for R_{Cr-F} = 1.89 Å (Figure 1) [16].

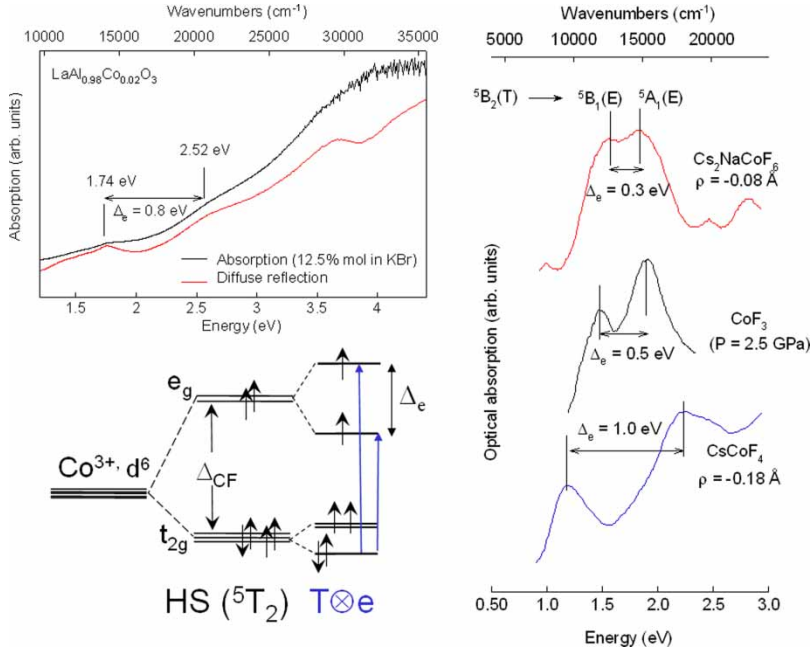


Figure 2. Absorption spectrum of Co^{3+} -doped LaAlO_3 at ambient conditions (left) and $\text{Cs}_2\text{NaCoF}_6$ [5], CsCoF_4 [5] and CoF_3 [present work]. The arrows in the one-electron level diagram indicate the observed transitions.

Figure 2 shows the absorption spectra of Co^{3+} -doped LaAlO_3 and several Co^{3+} fluorides. The absorption bands of Co^{3+} -doped LaAlO_3 and CoF_3 are mounted on an intense background due to the light scattering in compressed powders. Background subtraction allows us to separate the two contributions and obtain the absorption bands due to Co^{3+} . Their position and structure are similar to those observed in other Co^{3+} fluorides [5,6]. The spectra show one absorption band with two components located at 1.53 and 1.83 eV in $\text{Cs}_2\text{NaCoF}_6$ [5], 1.39 and 1.81 eV in Li_3CoF_6 [6], 1.17 and 2.18 eV in CsCoF_4 [5], and 1.45 and 1.89 eV in the reported CoF_3 . The absorption bands are related to crystal-field transitions of Co^{3+} from the HS ground state (5T_2) to the excited state 5E split by the JT distortion ($T \otimes e$). Note that the splitting in CoF_3 ($\Delta_e = 0.45$ eV) is similar to that measured in Li_3CoF_6 (0.42 eV) [6] or $\text{Cs}_2\text{NaCoF}_6$ (0.30 eV) but lower than in CsCoF_4 (1.01 eV). As indicated in [5], besides the JT effect, CsCoF_4 provides an additional contribution to Δ_e due to crystal anisotropy [5]. The CoF_3 spectrum is consistent with a HS (5T_2) ground state, which experiences a significant JT effect yielding a e_g -splitting Δ_e similar to that attained in other Co^{3+} fluorides. From Equation 1, we estimate a JT distortion: $\rho \approx -0.09 \text{ \AA}$.

A similar band structure is observed in Co^{3+} -doped LaAlO_3 at ambient conditions (Figure 2). The bands at 1.74 and 2.52 eV are consistent with $\Delta_e = 0.8$ eV and $\Delta_{\text{CF}} = 2.1$ eV [15]. The crystal-field splitting Δ_{CF} indicates that the system is beyond the SCO (1.8 eV) [17], and thus the electronic ground state must correspond to the LS 1A_1 state as was confirmed by magnetic measurements. Co^{3+} is non-magnetic (LS: $S = 0$) at low temperatures and its magnetic moment increases with temperature due to thermal population of either IS ($S = 1$) or HS ($S = 2$) states. A similar behaviour was observed in the neat compound LaCoO_3 [10]. Nevertheless, the spectroscopic data reveal that the thermally populated state corresponds to the HS state (5T_2) rather than the IS state (${}^3T_{1,2}$). The latter state would exhibit a strong $E \otimes e$ JT effect yielding Δ_e splitting similar to, or larger than, the one attained in Mn^{3+} in fluorides [12,17] or in Ni^{3+} in oxides [15]. Therefore, the present results indicate that the HS state lies above the LS state, in agreement with conclusions given elsewhere [11].

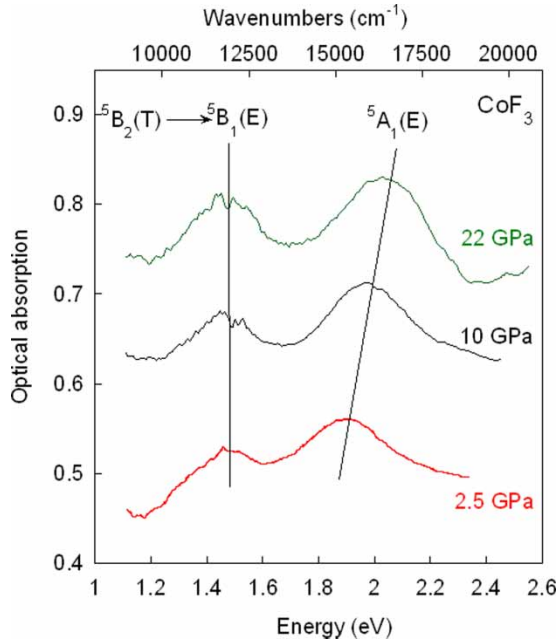


Figure 3. Variation of the absorption spectra of CoF_3 with pressure at room temperature. The bands are obtained after background subtraction.

The variation of the CoF_3 spectra with pressure through the SCO clarifies this behavior. Figure 3 shows the pressure dependence of the absorption spectra of CoF_3 . The JT-related splitting (Δ_e) is observed in the explored pressure range. The band at 1.89 eV experiences a significant blue shift of 0.2 eV as the pressure increases from 0 to 20 GPa according to an increase of the crystal-field strength, while the band at 1.45 eV sustains only a slight shift with pressure, showing that both Δ_{CF} and Δ_e increase with pressure. This result is not surprising since Δ_e can increase with pressure even if, as shown elsewhere [18], the JT distortion, ρ , reduces with pressure. The increase of Δ_{CF} and Δ_e as 0.009 and 0.005 eV/GPa, respectively, and the band enhancement at 1.9 eV above 10 GPa suggest that HS–LS crossover already occurs around this pressure. These results confirm the stability of the JT distortion with pressure for $\text{Mn}^{3+}(\text{E} \otimes \text{e})$ and $\text{Co}^{3+}(\text{T} \otimes \text{e})$ in fluorides as well as the pressure-induced HS to LS SCO.

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