Volume and bond length dependences of the electronic structure of 6-fold and 8-fold coordinated Co$^{2+}$ in pressure transformed CoF$_2$

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Abstract. This work reports an optical absorption study on CoF$_2$ under high-pressure conditions in the 0-80 GPa range. A recent structural study performed on the pressure-induced phase-transition sequence of CoF$_2$ reveals that this compound undergoes a structural transformation associated with a change of Co$^{2+}$ coordination from 6 (rutile type) to 8 (fluorite type) at 15 GPa, what implies a profound change in the Co$^{2+}$ electronic ground state associated with the inversion of $d$ orbitals from $(t_{2g}^5e_g)$ to $(e_g^4t_{2g}^3)$. This allows us to explore the Co$^{2+}$ electronic structure, and hence $10Dq$, as a function of the density and the Co-F bond length in both CoF$_6$ (rutile phase) and CoF$_8$ (fluorite phase) coordinations. The results are compared with those obtained in KCoF$_3$ (perovskite) in a wide range of Co-F distances (from 2.04 to 1.83 Å).

1. Introduction
There is a lack of experimental studies devoted to investigate the volume/density and bond length ($R$) dependencies of the crystal-field $d$-orbital splitting $e_g^4t_{2g}^3$ ($10Dq$) in transition metal ions (TM) occupying high-symmetry crystallographic sites. The situation is even harder if different coordination geometries are involved. Although experimental studies on $10Dq(R)$ have been usually performed at ambient pressure on series of TM compounds with different crystal structure and composition [1-4], rest-of-lattice and compositional effects can significantly mask the actual bond-length dependence of the TM electronic structure [5]. High-pressure spectroscopy solves out this problem since the electronic structure of a given compound can be measured as a function of pressure and eventually of $V$ and/or $R$ provided that its structure as a function of pressure is known.

Although pioneering works by Drickamer et al. [6] dealt with that problem in a lot of TM oxides and halides, correlations between $10Dq$ and $V$ were performed on TM-doped Al$_2$O$_3$ or MgO (TM: Ti,
Cr, V) since the equation of state was known only for few materials at that time [6, 7]. However, impurity systems pose a scale problem of whether the TM-ligand bond length and its variation with pressure are the same for the host (Al-O) and impurity (Cr-O) as for example in ruby (Al2O3: Cr3+) [4,8-10]. Recent high-pressure studies by optical spectroscopy provided such correlations in pure TM-ion compounds: NiO [11] and BiFeO3 [11, 12]. These studies gave evidence of 10Dq(V), and thus of 10Dq(R) dependences close to V5/3 and R5, respectively, given that in these compounds R(P) scales as V1/3(P), and therefore both dependences obey the same power law, in agreement with crystal-field theory (CFT) predictions. This result is quite surprising since CFT in the point charge approximation is very simple and does not take explicitly into account the TM-ligand bonding [13-15]. Although efforts to justify the R5 law have been done on the basis of ligand field theory [16,17] and by means of LCAO-type calculations, there is a lack of experimental studies aiming to validate whether CFT predictions on 10Dq apply for 1) different TM coordinations in the same crystal, i.e. 6-fold and 8-fold cubic coordinations in CoF2; 2) the same coordination in different crystals, i.e. 6-fold coordination in CoF2 and KCoF3; and 3) a coordination change, i.e. 10Dq(6-fold)/10Dq(8-fold) for the same R value.

This work reports an optical absorption study on CoF2 under high-pressure conditions in the 0-80 GPa range. A recent structural study [18] performed on the pressure-induced phase-transition sequence of CoF2 reveals that this compound undergoes a structural transformation associated with a change of Co2+ coordination from 6 (rutile type) to 8 (fluorite type) at 15 GPa, what implies a profound change in the Co2+ electronic ground state associated with inversion of d orbitals splitting from (t2g5eg2) to (eg4t2g3). This different ground state electronic configuration allows us to explore clearly the Co2+ electronic structure, and hence 10Dq, as a function of the density and RCo-F in the two coordinations: CoF6 (rutile phase) and CoF8 (fluorite phase), taking the structural data reported elsewhere [18]. The results will be compared with those obtained in KCoF3 where the 6-fold coordination of Co2+ in the perovskite structure is stable up to 80 GPa, thus providing the widest 10Dq(R) range ever measured in TM ions.

2. Experimental

2.1. Crystal structure and x-ray diffraction

Single crystals of CoF2 and KCoF3 grown by the Bridgman method according to methods described elsewhere [18]. At ambient conditions CoF2 crystallizes in the tetragonal space group P42/mnm (rutile phase) [18] and KCoF3 in the cubic Pm3m (perovskite phase) [19,20]. The evolution of the crystal structure of KCoF3 with pressure was studied by angle dispersive x-ray diffraction (AXRD) on powdered samples using the 12.2.2 beamline at the Advance Light Source (ALS). Pressure was applied by means of a symmetric piston cylinder Diamond Anvil Cell (DAC). High pressure experiments on polycrystalline CoF2 were performed in the Materials Science and Powder Diffraction beamline (BL04) at ALBA synchrotron using a Boehler-Almax DAC. In all experiments samples were loaded with several Ruby spheres (10 μm diameter) as pressure gauge [21] using methanol-ethanol-water and silicone oil as pressure transmitting media.

2.2. Optical Absorption and Raman Spectroscopy

Optical absorption and Raman experiments were performed on single-crystal plates of CoF2 (90x80x14 μm3) and KCoF3 (100x80x20 μm3) were used for high-pressure optical absorption experiments. The optical spectroscopy experiments were carried out in membrane and Almax-Boehler DACs. 200-μm-thick Inconel gaskets were preindented to 40 μm. 200-μm-diameter holes were perforated with a BETSA motorized electrical discharge machine. The DAC was loaded with a single crystal plate of CoF2 or KCoF3 and ruby microspheres (10 μm diameter) as pressure probes [21] using silicon oil as pressure-transmitting medium.

Optical absorption under high-pressure conditions was performed on a prototype fiber-optics microscope equipped with two 25× reflecting objectives mounted on two independent x-y-z translational stages for the microfocus beam and the collector objective, and a third independent x-y-z
translational stage for the DAC holder. Optical absorption data and images were obtained simultaneously with the same device [22]. Spectra in the UV-VIS and NIR were recorded with Ocean Optics USB 2000 and NIRQUEST 512 monochromators using Si- and InGaAs-CCD detectors, respectively.

Unpolarized micro-Raman scattering measurements were performed with a triple monochromator Horiba-Jobin-Yvon T64000 spectrometer in subtractive mode backscattering configuration, equipped with an Horiba Symphony liquid-nitrogen-cooled CCD detector. The 514.5-nm and 647-nm lines of an Coherent Innova 70 Ar+-Kr+ laser were focused on the sample with a 20× objective for micro-Raman, and the laser power was kept below 4 mW in order to avoid heating effects. The laser spot was 20 μm in diameter and the spectral resolution was better than 1 cm⁻¹. The Raman technique was used in combination with X-ray diffraction to check the sample structure through the characteristic first-order modes in CoF₂ [18] and absence of first-order modes in KCoF₃ as well as to determine structural phase-transition pressures. The Raman high-pressure experiments were performed on the same CoF₂ and KCoF₃ single crystals employed in the optical absorption measurements.

Figure 1. Optical absorption spectra of CoF₂ and KCoF₃ at ambient pressure and 290 K and low temperature (13 and 18 K, respectively). Spectra are normalized to the absorption coefficient. The peak energies are compared with those predicted by the Tanabe-Sugano diagram for octahedral Co²⁺ (3d⁷): Racah (B) and crystal-field (10Dq) parameters obtained by fitting the experimental energies to the calculated energies are: Δ = 0.950±0.005 eV and B = 0.105±0.003 eV for KCoF₃; and Δ = 0.962±0.005 eV and B = 0.107±0.003 eV for CoF₂ (Δ/B = 9).
3. Results and discussion

Figure 1 shows the electronic absorption spectrum of CoF$_2$ and KCoF$_3$ at ambient pressure, as well as the Tanabe-Sugano and corresponding $B$ and 10$Dq$ parameters, which account for the Co$^{2+}$ transition energies. Both compounds exhibit a similar spectrum as it mainly corresponds to the CoF$_6$ coordination unit with similar Co-F bond distances: $R = 2.042$ and 2.035 Å [23,24]; and associated CF parameters: $B = 0.107$ and 0.105 eV; and 10$Dq = 0.962$ and 0.950 eV, for CoF$_2$ and KCoF$_3$, respectively. Interestingly, the similarity of spectra strengthen the relevance of CoF$_6$ to account for the CF electronic structure of Co$^{2+}$ beyond other ionic shells of the crystal, the influence of which seems to be much weaker than the first F$^-$ shell in spite of the distinct crystal structure: rutile (CoF$_2$) and perovskite (KCoF$_3$). However, the slightly bigger 10$Dq$ of CoF$_2$ with respect to KCoF$_3$ contrasts with the shorter Co-F distance in KCoF$_3$ must be ascribed to rest-of-the-lattice CF effects beyond CoF$_6$, which is estimated to be less than 4% of 10$Dq$.

Figure 2. Pressure dependence of the optical absorption spectrum of CoF$_2$. Spectra correspond to rutile-type structure (blue), orthorhombic (green) with 6-fold coordinated Co$^{2+}$, and to fluorite-type phase (red) with 8-fold coordinated Co$^{2+}$ [18]. The bands correspond to crystal-field transitions from the electronic ground state $^4T_1$(F) in CoF$_6$ and $^4A_2$(F) in CoF$_8$ to different excited states $\Gamma_i$ according to the assignment given in the corresponding Tanabe-Sugano diagrams for $d^7$ and $d^3$, respectively. The energy of the $\Gamma_i$ state is represented as a function of the crystal-field splitting and are both given in units of the Racah parameter $B$ [24]. Colour representing $\Gamma_i$ state has been maintained in both figures. The two sets of experimental points in the Tanabe-Sugano diagram denote the low pressure and high-pressure limits in both 6-fold and 8-fold coordinations. The variations of 10$Dq$ and $R$ in the corresponding pressure range are also indicated. Interestingly, the CoF$_6$ (rutile)
to CoF$_4$ (fluorite) change of coordination taking place in CoF$_2$ at 15 GPa induces a drastic change in the absorption spectrum which is associated with the corresponding change of electronic configuration (from $d^7$-like to $d^3$-like) affecting the ground and excited states, and hence the absorption spectra. However such an abrupt change is not observed in KCoF$_3$ since the CoF$_6$ octahedral coordination is stable in the 0 - 80 GPa range as indicated by AXRD experiments whose $V(P)$ data are represented in figure 3 (right). Consistently, the absorption spectrum of KCoF$_3$ in the whole pressure range is concomitant with an electronic configuration $d^7$ and thus the experiment provides the widest $10Dq(R)$ range explored ever in Co$^{2+}$.

**Figure 3.** Variation of the absorption spectrum of KCoF$_3$ with pressure (left) and of the perovskite cell volume $V(P)$ (right). The peak energies are compared with those predicted by the Tanabe-Sugano diagram. The $B$ and $10Dq$ parameters obtained by fitting the experimental energies $E(P)$ to the calculated crystal-field energies are: $10Dq = 0.960\pm0.005$ eV and $1.67\pm0.01$ eV, and $B = 0.105\pm0.003$ and $0.100\pm0.003$ eV for KCoF$_3$ at 0 and 67 GPa, respectively. The Tanabe Sugano-diagram compares the $10Dq/B$ range swept by pressure for CoF$_6$ in KCoF$_3$ (red dots): $10Dq/B = 10 \rightarrow 18$. The corresponding $R$ variation obtained from the Equation of State $V(P)$ is indicated.

In general, pressure-induced phase transitions in both CoF$_2$ and KCoF$_3$ affect the electronic spectra as evidenced through their $10Dq(P)$ behaviour (figure 4). The different slope of $10Dq(P)$ exhibited by the perovskite KCoF$_3$ unravels the effect of a cubic ($Pm-3m$) to orthorhombic ($Pnma$) second-order phase transition at 24 GPa. Such a phase transition, which is associated with rotations of the CoF$_6$ octahedra, keeps the 6-fold octahedral coordination of Co$^{2+}$ in the high-pressure orthorhombic phase, and thus $10Dq$ varies continuously at the phase transition, although its pressure dependence is
different in each phase. This pressure behaviour contrasts with that exhibited by CoF$_2$, whose $10Dq(P)$ values show a peculiar pressure dependence through which the corresponding $10Dq(R)$ have been derived using the available XRD and XAS structural data reported elsewhere [18]. In CoF$_2$, pressure induces an increase of $10Dq$ from 0.96 to 1.06 eV in the 0-6 GPa (rutile phase), whereas at 15 GPa, it abruptly decreases by -0.3 eV along with the 6- to 8-fold coordination change. Above 15 GPa, $10Dq$ increases at a rate of 9 meV GPa$^{-1}$ in the fluorite phase, and at 4.4 meV GPa$^{-1}$ beyond 44 GPa in the cotunnite phase [18].

\[10Dq(P)\]

\[10Dq(R)\]

\[R-P\]

\[R-n\]

\[n=5.1\pm0.3\]

\[n=6.0\pm0.2\]

\[9/8\]

\[ab initio\]

\[DFT\]

\[CFT\]

\[CoF_2\]

\[CoF_3\]

\[XRD\]

\[XAS\]

\[R(P)\]

\[10Dq(R)\]

\[10Dq(P)\]

\[P4_2/mnm\]

\[Pbca\]

\[Fm3m\]

\[Pnma\]

\[Pm3m\]

\[Pnma\]

\[19 meV/GPa\]

\[7 meV/GPa\]

\[\Delta_b=0.96 eV\]

\[P4_2/mnm\] ↔ \[Pbca\] ↔ \[Fm3m\] (fluorite) ↔ \[Pnma\] (cotunnite) in CoF$_2$, and \[Pm3m\] ↔ \[Pnma\] (perovskite) in KCoF$_3$, respectively.

4. Concluding remarks

The knowledge of EOS and \(R(P)\) in the two investigated compounds from XRD and XAS (Figure 3) [18,20] allows us to derive $10Dq(R)$ from the corresponding $10Dq(P)$. A noteworthy result concerns the regular variation of $10Dq(R)$ in CoF$_6$ and CoF$_8$ with respect to variations of $10Dq(P)$ that show anomalies at the phase transitions in both CoF$_2$ and KCoF$_3$. Such anomalies are concurrent with similar anomalies in $R(P)$ thus highlighting the suitability of $R$ (and neither $V$ nor density) to properly describe pressure-induced variations of $10Dq$. Furthermore, $10Dq(R)$ obeys a potential law as $R^n$ with $n$ close to 5 in both compounds. In particular, we get an exponent $n = 5.1\pm0.3$ in KCoF$_3$, in an $R$ range of 12% whereas in CoF$_2$ $n = 5.0\pm0.1$ (rutile phase) and $n = 6.0\pm0.2$ (fluorite phase) as deduced from their relative changes of $R$ and $10Dq$ in the explored $R$-ranges (figures 2 and 3).

The reliability of CFT to fairly account for $R$-dependence of $10Dq$ is also confirmed through the relative $10Dq$ values obtained for CoF$_6$ and CoF$_8$ in CoF$_2$ at the same Co-F distance, $R = 2.04$ Å, as $10Dq(oct)/10Dq(cub) = 1.10$. Its similitude with the theoretical value of 9/8 supports CFT predictions to accurately describe experimental $10Dq(R)$.

Finally, this study constitutes a reference system to validate \textit{ab initio} methods aiming to calculate electronic structure (including excited states) of TM ions besides of well-suited DFT methods to calculate crystallographic and vibrational structures.

Acknowledgments

Financial support from the Spanish Ministerio de Economía y Competitividad (Project No. MAT2015-69508-P) and MALTA INGENIO-CONSOLIDER 2010 (Ref. No. CDS2007-0045) is acknowledged.
The ALS is supported by the Director, Office of Science, Office of Basic Energy Sciences of the US Department of Energy, under Contract No. DE-AC02-05CH11231.

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