Change from Fluorescence to Phosphorescence and Tuning the Pseudo-Jahn−Teller Effect with Pressure for $(NH_4)_3[CrF_6]$

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Emission from the Cr^{3+} ion in an O_h ligand field and in lower symmetry ligand fields typically is fairly sharp, has well-defined vibronic structure, and derives from the spin-forbidden (or phosphorescent) ${}^4A_{2g} \leftarrow {}^2E_g$ transition.[1,2] Octahedrally coordinated Cr^{3+} ions in a very weak ligand field, however, also can exhibit a broad, unstructured ${}^4A_{2g} \leftarrow {}^4T_{2g}$ fluorescence, an example of which is seen in the solid $(NH_4)_3[CrF_6]$. In fact, there are many chromium complexes, such as $[Cr(H_2O)_6]^{3+}$ and $[Cr(urea)_6]^{3+}$, that exhibit emission from both states; i.e., they both phosphoresce and fluoresce.[2−4] Although the fluorescence-to-phosphorescence ratios in these dual emitting systems vary dramatically with temperature,[5] the variations are due primarily to Boltzmann factors, which describe the relative thermal populations between the two excited states.

We report here the pressure-induced change of the emitting state of $(NH_4)_3[CrF_6]$ from a ${}^4T_{2g}$ fluorescent state to a mixed state by means of the pseudo-Jahn−Teller effect, and then finally to a ${}^2E_g$ phosphorescent state over the pressure range 0−12.3 GPa. We believe that this is the first time an emitting state's spin character has been changed completely by the application of pressure. Figure 1 shows the change in the emission spectrum of $(NH_4)_3[CrF_6]$ with increasing pressure at 22 K. A pressure increase from 0 to 2.1 GPa blue-shifts the ${}^4T_{2g}$ state 0−0 from 14 319 to 14 554 cm^{-1} (112 cm^{-1}/GPa), while the change from 2.1 to 7.1 GPa shifts this state to only 14 855 cm^{-1} (60 cm^{-1}/GPa). The structure that appears on the 2.1 GPa spectrum evidently is due to defect sites induced by loading and unloading since it depended on sample history and was not reproducible.[6] Corresponding changes for the centroid of this quartet emission are 12 984 cm^{-1} (0 GPa), 13 312 cm^{-1} (2.1 GPa), and 13 605 cm^{-1} (7.1 GPa) (see Figure 2). Note the emergence of a shoulder on the high-energy side of the quartet centroid in the 7.1 GPa spectrum in Figure 1. Although the shift of quartet emission from Cr^{3+} never has been reported as a function of pressure, the pressure-induced shift of quartet *absorption* has been reported[7] for ${}^4A_2 \rightarrow {}^4T_2$ of $Al_2O_3{:}Cr^{3+}$ (ruby) and is 91 cm^{-1}/GPa over a similar pressure range. Increasing pressure to ~7.8 GPa[8] results in a further blue shift of the quartet emission band, but more significantly, there is an onset of vibronic structure on the normally structureless quartet emission (see Figure 1). The 0−0 for this new emission appears at 14 722 cm^{-1}, which is 133 cm^{-1} to *lower* energy than the 0−0 for the quartet emission at 7.1 GPa. Moreover, the vibronic structure for this new emission extends beyond any structure normally present for ${}^2E_g$ emission in high-symmetry Cr^{3+}. This new emission seems to derive from a strong coupling of the vibronic structure reminiscent of reported vibrational structure[9] for the ${}^4B_{1g} \leftarrow {}^2E_g$ emission from *trans*-$[Cr(en)_2F_2]I$ (en = ethylenediamine), which extends some 1300 cm^{-1} from its origin at 13 044 cm^{-1}.

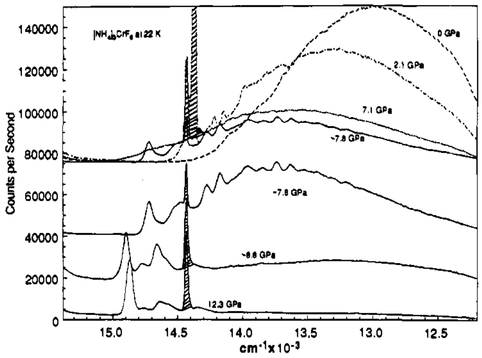

Figure 1. Pressure-dependent luminescence spectra of $(NH_4)_3[CrF_6]$ measured at 22 K in a diamond anvil cell (DAC) with 632.8 nm He/Ne laser excitation. Pressures represented with the symbol ~ are approximated as described in text. Hatched peaks are due either to the 1332 cm^{-1} diamond Raman line or to the ruby phosphorescence used to measure pressure.

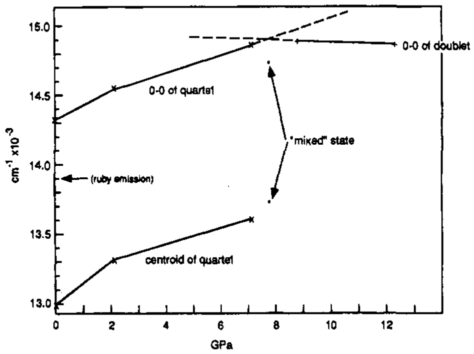

Figure 2. Plot of the energies of the quartet (×), mixed state (*), and doublet (+) emissions as a function of pressure. The shift vs pressure undoubtedly varies in a continuous manner below 7.1 GPa, but we have approximated it by two straight lines.

Further increasing pressure to ~8.8 GPa[10] diminishes the ${}^4T_{2g}$ fluorescence band, and a well-defined ${}^2E_g$ phosphorescence appears with a 0−0 at 14 896 cm^{-1}, now some 184 cm^{-1} blue-shifted from the 0−0 of the mixed-state emission. At the final pressure shown, 12.3 GPa, this ${}^2E_g$ phosphorescence then red-

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(6) Additional support for this defect site explanation comes from our 0 GPa reference spectra on $(NH_4)_3[CrF_6]$. In a select few samples that had never been pressurized, some non-reproducible structure was observed on the band envelope of the 0 GPa fluorescence spectra. Pressurization and release of these samples totally removed this structure. The resulting broad structureless emissions were identical to the 0 GPa spectrum shown in Figure 1. We ascribe this phenomenon to defect site removal via pressure annealing of the crystals.

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(8) Since we put no ruby in this sample, this pressure is based on the intersection of the extrapolated shifts, shown in Figure 2 as dashed lines, for the doublet and quartet emissions.

(9) Flint, C. D.; Matthews, A. P. *J. Chem. Soc., Faraday Trans. 2* **1974**, *70*, 1307−1315.

(10) No ruby was placed in this sample. Since the pressure shifts in the quartet emission of ruby and $(NH_4)_3[CrF_6]$ are similar, we assume that the shifts in the doublet emissions will also be similar. We therefore use the ruby doublet pressure shift value of 0.012 38 GPa/cm^{-1} to calculate the ~8.8 GPa pressure of this sample doublet emission by extrapolating back from the known 12.3 GPa doublet emission of the sample.

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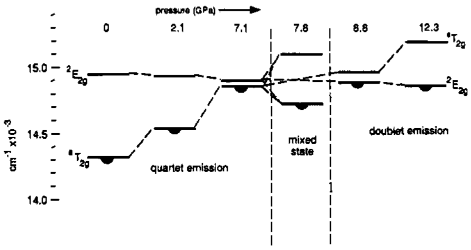

Figure 3. Relative ordering of the doublet and quartet emitting states for the various pressures.

shifts to 14 624 cm^{-1}. A report of the low-temperature emission of $K_3[CrF_6]$ has shown[11] ^2E_g emission below 16 K with structure similar to ours, but with an origin at 13 553 cm^{-1}. This doublet emission gave way to an unstructured quartet at higher temperatures, with a 0–0 close to 14 000 cm^{-1}, and so represents a corresponding case of tuning between the quartet and doublet states with temperature.[12]

Our results have straightforward interpretation outside of the pressure regime of the "mixed" state. The F^- ligand, a weak field ligand under ambient pressure conditions, effectively becomes a strong field ligand with the application of pressure. Pressure increases the crystal field splitting energy Δ_0 and blue shifts the $^4T_{2g}$ state (Figure 3), just as shown in d^3 Tanabe–Sugano diagrams.[13] The ^2E_g state slightly red-shifts with increasing pressure, as this spin-flip state depends on factors besides Δ_0.[14,15] Since the $^4T_{2g}$ state starts out at a lower energy than the ^2E_g and blue-shifts with increasing pressure, it eventually will cross the ^2E_g state, which is red-shifting with increasing pressure, and the ^2E_g state then will become the lowest state (Figure 3). Since these two electronic states belong to different irreducible representations,[16] they simply could cross without interaction with increasing pressure. For our system we predict this crossing to occur at 14 900 cm^{-1}. However, there is a narrow pressure range over which these two states display a great deal of mixing, as shown by the spectrum for ~7.8 GPa in Figure 1.

An explanation for this mixing lies with the *pseudo*-Jahn–Teller effect (PJTE),[17] where an accidental degeneracy (or near degeneracy) of electronic states can result in a spontaneous distortion of a molecule to remove that "degeneracy." For this effect, it is important to recognize that the distorted excited state emission will have the same *frequencies* in its progression as those from the doublet state, since they both decay to the same ground state, but different relative *intensities* among the components because of different Franck–Condon factors. Our case corresponds to a strong PJTE limit, since the molecule undergoes an asymmetric distortion. Therefore, we consider only linear terms of the interaction for the PJTE, $\Delta < F^2/K$, where 2Δ is the energy difference between the states, K is the force constant for the mode involved in the distortion, and F is the nondiagonal vibronic interaction matrix element. Thus, it is clear that if we can adjust 2Δ to an arbitrarily small value by adjusting the pressure, even a very small interaction term F can lead to a significant excited state distortion. The analogy to *trans*-$[Cr(en)_2F_2]I$ is clear; this complex already is distorted by the asymmetry of the coordination sphere. We assume that this is also the source of the highly structured defect emission observed in $K_3[CrF_6]$, and the defect must involve a distorted Cr^{3+} site.[11,12]

The main components of the progression for the mixed state at ~7.8 GPa are 245 (ν_5, t_{2g}), 446 (ν_2, e_g), 547 (ν_1, a_{1g}), 762 (ν_3, t_{1u}) cm^{-1}, $2\nu_2$, $\nu_1 + \nu_2$, and $2\nu_1$ while those for the doublet emission at 12.3 GPa are 106 (ν_6, t_{2u}), 238 (ν_5, t_{2g}), 298 (ν_4, t_{1u}), and 525 (ν_1, a_{1g}) cm^{-1}. These bands are assigned according to the analogous $[AlF_6]^{3-}$ and $[CrCl_6]^{3-}$ ions.[18] The similarities of the frequencies of these bands between the two emissions coupled with the completely different intensity distributions among the various features strongly suggest that both emissions are to the same ground state (i.e., are not due to different sites) and that the "mixed" excited state has a very different geometry from either the quartet or the doublet states. Furthermore, the notable enhancement of the 446 (ν_2, e_g) and 547 (ν_1, a_{1g}) cm^{-1} fundamental, overtone, and combination bands for the mixed state suggests that these modes are the coordinates along which the ion distorts, although a more detailed analysis will be required to verify this. Note that for the PJTE, unlike the normal Jahn–Teller effect, there are no symmetry restrictions on the vibrational modes (or combinations thereof) that can be involved. Even an *ungerade* mode is possible. The ν_2 mode is a D_{4h} distortion, which is consistent with the symmetry of the *trans*-$[Cr(en)_2F_2]I$ mentioned above. This molecule also exhibits extended vibronic structure in its emission.

The luminescence spectra at 22 K of $(NH_4)_3[CrF_6]$ were obtained at various pressures using a Merrill-Bassett diamond anvil cell (DAC).[19] The samples were compressed using cyclohexane as a hydrostatic fluid and excited with the 632.8 nm line of a 25 mW Aerotech He/Ne laser. This line falls near the $^4A_{2g} \rightarrow {}^4T_{2g}$ absorption maximum of $(NH_4)_3[CrF_6]$ at 0 GPa.[3] Pressure calibration in the DAC was achieved by measuring the R_1 line shift of ruby phosphorescence at 22 K.[20] Luminescence was detected by a Spex 1680 0.22 m double monochromator equipped with a Hamamatsu R928 PMT operating in the photon-counting mode. The DAC was cooled to 22 K in an Air Products Displex cryogenic refrigerator. Elemental analysis of $(NH_4)_3[CrF_6]$, prepared by the method of Schläfer et al.,[3] was performed by Galbraith Laboratories. All of the pressure effects reported here are reversible and reproducible on the same or different samples. With the exceptions[6] noted, luminescence spectra from depressurized samples are virtually identical to spectra from samples of $(NH_4)_3[CrF_6]$ that never were subjected to high pressures.

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(12) Koglin and Krasser (ref 11) also reported a structured quartet fluorescence with a 0–0 at 12 812 cm^{-1}, some 741^{-1} to the red of the doublet state at 4.2 K. They argued for a simultaneous emission from both states, despite the fact that none of the frequencies in the quartet progression corresponded to frequencies of the doublet emission. We suggest that this structured quartet emission was in fact due to a defect site, and not an intrinsic property of the compound.

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(16) In the double group representations of the $^4T_{2g}$ and ^2E_g states there is a common symmetry component through which spin–orbit-induced mixing could, in principle, occur. However, the primary effect of the pressure perturbation at the molecular level is to induce distortions in vibronic states. We therefore favor a vibronic mixing model.

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