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Pressure and temperature dependence of chromium photoluminescence in K_2NaGaF_6:Cr^{3+}

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Photoluminescence spectra and lifetimes of K_2NaGaF_6:Cr^{3+}, measured as functions of pressure and temperature, reveal a pressure-induced transition from broad-band fluorescence to narrow-band phosphorescence.

Low-crystal-field octahedral complexes of Cr^{3+} in solids exhibit broad-band $(^4T_{2g} \rightarrow {}^4A_{2g})$ fluorescence, rather than the narrow-band $(^2E_g \rightarrow {}^4A_{2g})$ phosphorescence of high-field complexes such as ruby. This contrasting behavior has been demonstrated previously in a variety of host crystals which provide a range of octahedral crystal fields.[1] In the present investigation, photoluminescence spectra and lifetimes of the chromium-doped ordered perovskite K_2NaGaF_6:Cr^{3+} were measured as a function of temperature and pressure in a diamond-anvil cell. The possibility of a pressure-induced transition from low-field to high-field behavior in a single host crystal is established by these measurements.

A single crystal of random orientation and appropriate size was selected from a powder sample of $K_2NaGa_{0.99}Cr_{0.01}F_6$, inserted in the diamond-anvil cell[2] together with a smaller chip of 0.55% ruby, and immersed in a hydrostatic pressure medium consisting of a 4:1 methanol-ethanol solution. Excitation light was provided by an Omnichrome helium-cadium laser with approximately 5 mW output at a wavelength of 442 nm. The pressure was monitored by the ruby R_1 line shift.[3] Approximate lifetime measurements were made by chopping the exciting light at 450 Hz. Low-temperature measurements were accomplished by mounting the diamond-anvil cell in vacuum in a cold-finger Dewar, equipped with optical windows. The temperature was controlled by adjusting the flow rate of cooled nitrogen gas, and monitored by a thermocouple.

The photoluminescence spectra of K_2NaGaF_6:Cr^{3+} at ambient temperature are shown in Fig. 1 as a function of pressure. The rapid shift of the broad emission band to shorter wavelength with increasing hydrostatic pressure is accompanied by the progressive development of a highly structured emission spectrum whose distinguishable features appear to remain at fixed wavelengths; these changes are accompanied by an increase in radiative lifetime from approximately 300 μsec at ambient pressure to over 1 msec at high pressure.

The distinction between low-field and high-field octahedral chromium complexes is illustrated by the configuration-coordinate diagram shown in Fig. 2. The Frank-Condon offset of the $^4T_{2g}$ state is a direct consequence of the dependence of its crystal-field splitting from the $^4A_{2g}$ ground state on the configuration coordinate.[1] The separation of the ^2E_g and $^4A_{2g}$ states, on the other hand, is attributable primarily to the exchange interaction and is thus relatively insensitive to the crystal field.[4,5] For weak crystal fields, the minimum energy of the $^4T_{2g}$ excited state lies below that of the ^2E_g state, and the photoluminescence spectrum at room temperature is a broad, featureless multiplicity-allowed fluorescence band. For stronger crystal fields, the minimum energy of the ^2E_g state lies lower and a highly structured, multiplicity-forbidden phosphorescence spectrum is observed. The pressure dependence of the photoluminescence spectrum shown in Fig. 1, as well as the observed changes in radiative lifetime, can be explained in terms of a progressive enhancement of the crystal field with increasing pressure,[6] culminating in a transition from low-field to high-field behavior. The broad-band fluorescence persists to higher pressures with diminishing intensity, as a consequence of thermal population of the $^4T_{2g}$ state from the ^2E_g state and its much shorter radiative lifetime. Note that the value of the crystal-field parameter $10Dq$ in the relaxed excited $^4T_{2g}$ state is less than that in the relaxed ^2E_g and $^4A_{2g}$ states; thus the complex can exhibit low- and high-field behavior simultaneously at temperatures for which both relaxed excited states are populated.

The effect of reduced temperature on the high-pressure (61-kbar) photoluminescence spectrum of K_2NaGaF_6:Cr^{3+} is illustrated in Fig. 3. The structured emission at 154 K is enhanced and its features are sharpened relative to that at

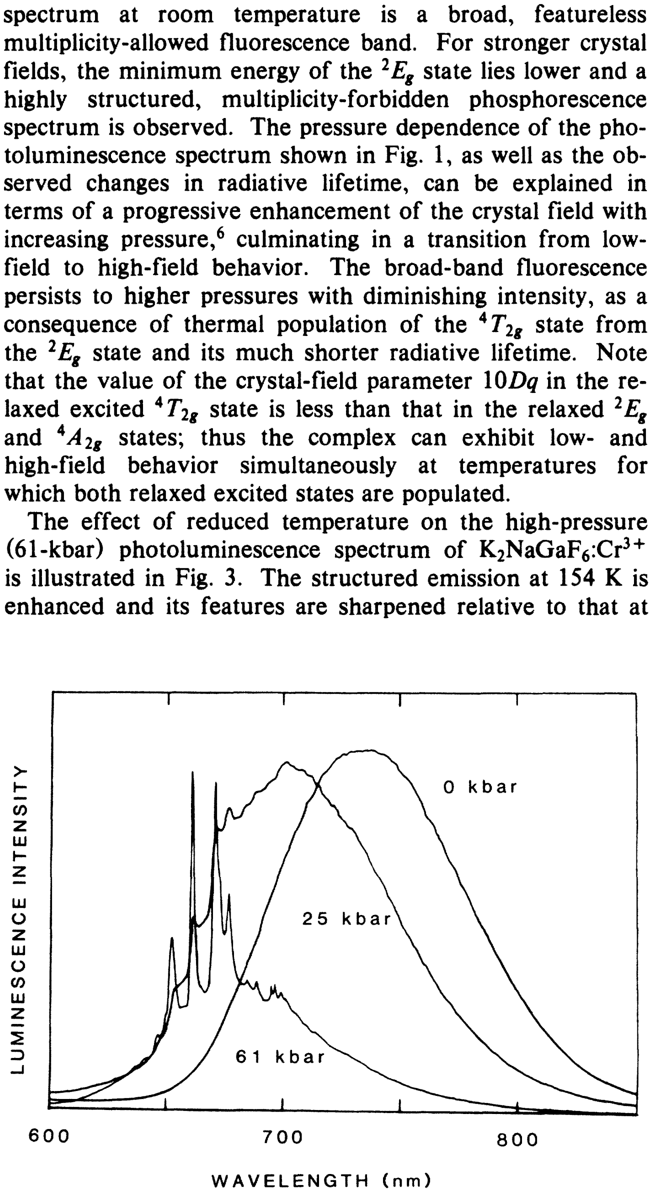

FIG. 1. Uncorrected photoluminescence spectra of K_2NaGaF_6:Cr^{3+}, with He-Cd laser excitation at 442 nm, as a function of pressure. Both a blue shift of the broad-band fluorescence and the development of a highly structured phosphorescence spectrum are in evidence. The three spectra shown were selected from 20 data sets in order to illustrate the major trends.

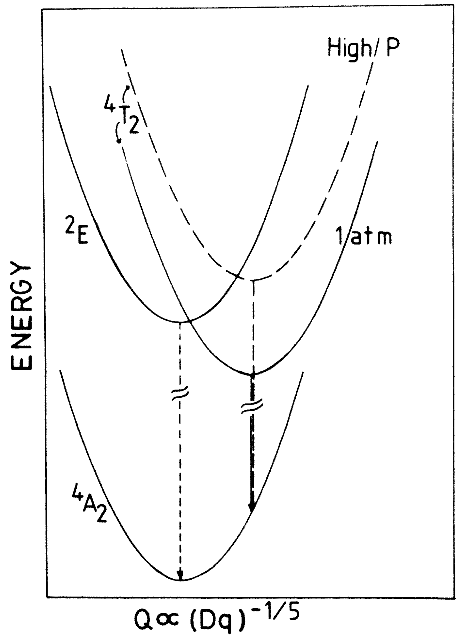

FIG. 2. Configuration-coordinate diagram for an octahedral complex of Cr^{3+}, neglecting spin-orbit interaction. The $^4T_{2g}$ adiabatic potential energy curve is represented by a solid curve at ambient pressure and a dashed curve at high pressure (61 kbar). The vertical dashed lines represent high-pressure luminescence.

300 K, while the underlying broad band is virtually absent.

Resolved vibronic structure of the emission spectrum of K_2NaGaF_6:Cr^{3+} at 4.2 K and ambient pressure[7] has been interpreted[8] by analogy with that of the high-field complex K_2NaAlF_6:Cr^{3+} in terms of normal modes of the $CrF_6{}^{3-}$ octahedral complex. The high-pressure low-temperature emission spectrum of K_2NaGaF_6:Cr^{3+} shown in Fig. 3 can be interpreted in similar fashion, since it bears an even closer resemblance to the spectrum of the aluminum compound. One striking difference, however, is the appearance of an anti-Stokes side band on the short-wavelength side of the zero-phonon line. Phonon energies inferred from the high-pressure spectrum are compared with those for ambient pressure in Table I. It is evident from the table that the vibration frequencies are increased by about 10% on the average at a pressure of 61 kbar. The observed intensity ratios of Stokes and anti-Stokes phonon replicas are 7.8 for the t_{2u} mode and 12 for the t_{2g} mode, in close agreement with the expected ratios given by $\exp(-\hbar\omega/k_BT)$.

Changes in the relative intensities of phonon replicas, as well as in their frequencies, are observed in the high-pressure spectrum of Fig. 3 with respect to the ambient-pressure spectrum.[7] These changes are attributed to the fact that the high-pressure luminescence originates in a relatively pure ^2E_g state, while that at ambient pressure and low temperature appears to originate in a $^4T_{2g}$ state which is strongly mixed with the ^2E_g state by spin-orbit coupling. Since the crossing of adiabatic potential energy curves is avoided, the low-temperature spectrum evolves continuously with pressure.

The crystal-field parameter $10Dq$ appropriate to the relaxed $^4T_{2g}$ excited state, as estimated from the peak wavelength of the uncorrected broad fluorescence band at room temperature, increases from 13 700 ± 100 cm^{-1} at ambient pressure to 14 800 ± 100 cm^{-1} at 61 kbar. This observed 8% increase in $10Dq$ at 61 kbar implies a 1.6% reduction in chromium-ligand distance on a point-charge model ($10Dq \propto Q^{-1/5}$).[6] A slight increase is observed in the energy of the zero-phonon line, from 15 045 ± 2 cm^{-1} at ambient pressure and 4.2 K[7] to 15 156 ± 2 cm^{-1} at 61 kbar and 154 K, in contrast with the pressure-induced red shift of the *R* lines observed in both ruby[3] and alexandrite[9] due to reduction of the Racah parameters *B* and *C*.[6] This anom-

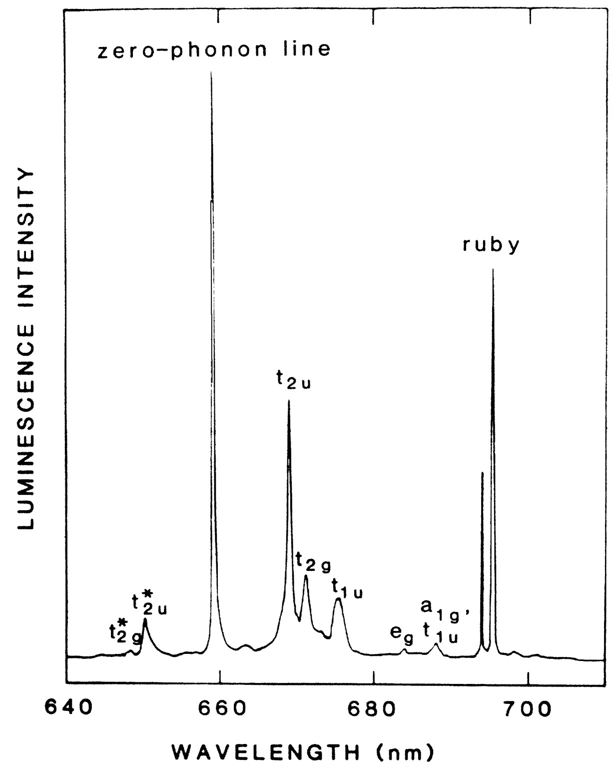

FIG. 3. Photoluminescence spectrum of K_2NaGaF_6:Cr^{3+} at 61 kbar and 154 K. The magnetic-dipole origin (zero-phonon line of the $^2E_g \rightarrow {}^4T_{2g}$ transition) and its phonon replicas are identified by comparison with the emission spectrum of K_2NaAlF_6:Cr^{3+} at 4.2 K and ambient pressure (Ref. 8). Replicas on the short wavelength side of the zero-phonon line, marked with an asterisk, are anti-Stokes lines.

TABLE I. Vibration frequencies (cm^{-1}) of the $CrF_6{}^{3-}$ complex in K_2NaGaF_6:Cr^{3+} at 61 kbar and 154 K. Frequencies are inferred from photoluminescence spectra and assigned by analogy with K_2NaAlF_6:Cr^{3+}.[a] Vibration frequencies for ambient pressure[a,b] are shown for comparison. All frequencies are accurate to ±3 cm^{-1}.

Mode pressure (kbar)	61	0
t_{2u} bend	217	200
t_{2g} bend	264	234
t_{1u} bend	361	329
e_g stretch	543	481
a_{1g} stretch	630	568
t_{1u} stretch	630	595

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alous blue shift of the zero-phonon line is attributed to the changing admixture of ${}^4T_{2g}$ and ${}^2E_g$ states with increasing pressure.

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