Influence of hydrostatic pressure on the Jahn–Teller effect in the ${}^{4}T_{2g}$ excited state of CrCl₆^{3–} doped Cs₂NaScCl₆

Oliver S. Wenger, Rafael Valiente,^{a)} and Hans U. Güdel^{b)}

Department für Chemie und Biochemie, Universität Bern, Freiestrasse 3, CH-3000 Bern 9, Switzerland

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The ${}^{4}T_{2g} \rightarrow {}^{4}A_{2g}$ luminescence of a 4.1% Cr³⁺ doped Cs₂NaScCl₆ crystal is studied as a function of hydrostatic pressure at room temperature and 15 K. The vibrational fine structure observed in the low-temperature variable pressure emission spectra is analyzed with a two configurational coordinate approach, involving the totally symmetric a_{1g} and the e_g Jahn–Teller normal coordinate. Increasing hydrostatic pressure is found to reduce the tetragonal distortion of the CrCl₆³⁻ unit in the electronic ${}^{4}T_{2g}$ state resulting from the Jahn–Teller effect. Additionally, pressure impedes expansion along the a_{1g} coordinate of the CrCl₆³⁻ complex upon ${}^{4}A_{2g} \rightarrow {}^{4}T_{2g}$ photo-excitation, and thus has a greater influence on the ${}^{4}T_{2g}$ excited state than on the ${}^{4}A_{2g}$ ground state. The absolute Cr³⁺–Cl⁻ average distance reduction upon increasing pressure is estimated using a simple point charge model. © 2001 American Institute of Physics. [DOI: 10.1063/1.1387038]

I. INTRODUCTION

In recent years, the optical spectroscopic properties of Cr³⁺ doped materials under high pressure have been of continuing interest. Indeed Cr^{3+} is probably the most thoroughly studied transition metal ion in the field of optical highpressure spectroscopy. So far, the research interests have been mainly twofold: So-called strong-field Cr³⁺ doped materials which exhibit sharp line emission from the electronic ${}^{2}E_{o}$ state have been studied with respect to their potential as optical pressure calibrants. The ruby (Cr³⁺:Al₂O₃) luminescence wavelength shift has become a standard method for pressure calibration.¹⁻³ In a search for alternatives to ruby, the materials alexandrite (Cr³⁺:BeAl₂O₄) and Cr³⁺ doped YAG $(Y_3Al_5O_{12})$ have been investigated.⁴⁻⁶ On the other hand numerous so-called weak-field Cr³⁺ doped materials were investigated with high-pressure techniques. In such systems there is a pressure induced crossover in the first excited state from ${}^{4}T_{2g}$ to ${}^{2}E_{g}$, and this manifests itself in a change from broad band to sharp line luminescence. Typical materials which exhibit this phenomenon at moderate pressures are fluorides such as Cr^{3+} :KZnF₃,⁷ Cr^{3+} :KMgF₃,⁸ and $Cr^{3+}:K_2NaGaF_6$,⁹ but also some selected oxides such as $(Gd_3Sc_2Ga_3O_{12})^{10}$ or Cr³⁺:GSGG Cr³⁺:LLGG (La₃Lu₂Ga₃O₁₂).¹¹ The extensive research efforts devoted to this area have motivated theoreticians to calculate and model the effect of pressure on the electronic structure of the Cr^{3+} ion.¹² Other aspects of Cr³⁺ spectroscopy under high pressure such as the effect of pressure on the exchange interaction in Cr³⁺ dimers have received significantly less attention.¹³ Another important aspect of Cr³⁺ which to our knowledge has not been investigated experimentally so far, is the influence of hydrostatic pressure on the Jahn-Teller effect in the electronic ${}^{4}T_{2g}$ state, although this effect has been

quite thoroughly investigated in various ambient pressurelow-temperature studies, involving materials such as $Cr(NH_3)_6(ClO_4)_2Cl$, ¹⁴ $Cr^{3+}:Cs_2NaYCl_6$, ¹⁵ as well as the title compound.¹⁶ Again, the relatively large amount of available experimental data has stimulated theoreticians to calculate the influence of the T \otimes e Jahn-Teller effect on the ${}^{4}T_{2g}$ potential surface.^{17,18} There are mainly two reasons why this effect has not been studied experimentally as a function of pressure up to now: First, the occurrence of sufficiently wellresolved vibrational fine structure in the $Cr^{3+} {}^{4}T_{2g} \rightarrow {}^{4}A_{2g}$ emission, an essential prerequisite for the Jahn-Teller analysis, is restricted to few selected host matrices. Second, most pressure studies done so far were performed at room temperature where the luminescence is broad and structureless. With $Cr^{3+}:Cs_2NaScCl_6$ we have chosen a material which is an efficient ${}^{4}T_{2g}$ emitter in the whole 10–300 K temperature range,¹⁶ allowing us to study the pressure dependent luminescence properties at cryogenic and ambient temperatures. At 15 K the luminescence exhibits vibrational fine structure, the influence of pressure on both the a_{1g} and e_{g} distortions of the $\operatorname{CrCl}_6^{3-}$ unit in the ${}^4T_{2g}$ excited state can be analyzed. The pressure induced blue shift of the ${}^{4}T_{2g} \rightarrow {}^{4}A_{2g}$ emission in this chloride lattice is compared to its pressure dependence in the fluorides and oxides, which are the materials that have so far been most frequently investigated with high-pressure techniques.

II. EXPERIMENT

The crystal growth is described in Ref. 16. For all measurements a crystal with an effective Cr^{3+} dopant concentration of 4.1% was used. The ambient pressure 15 K absorption spectrum was measured on a Cary 5*e* (Varian) spectrometer, and the sample was cooled in a He closedcycle cryostat (Air Products Displex). The ambient pressure 7 K emission spectrum was recorded using a sample with a size of about 5 mm×3 mm×3 mm. Excitation occurred with an air-cooled Ar⁺ laser (Ion Laser Technology, max. output

3819

^{a)}Permanent address: DCITIMAC, Facultad de Ciencias, Universidad de Cantabria, 39005 Santander, Spain.

^{b)}Electronic mail: hans-ulrich.guedel@iac.unibe.ch



FIG. 1. 15 K ${}^{4}A_{2g} \rightarrow {}^{4}T_{2g}$, ${}^{2}E_{g}$ absorption (right) and 7 K ${}^{4}T_{2g} \rightarrow {}^{4}A_{2g}$ emission spectrum (left) of 4.1% Cr³⁺:Cs₂NaScCl₆ at ambient pressure.

50 mW) at 514.5 nm. The detection system consisted of a 3/4 m single monochromator equipped with a 750 nm blazed grating (600 grooves/mm) and a liquid nitrogen cooled Ge detector (ADC 403L) connected to a lock-in amplifier (SR 830). Sample cooling was achieved with a He gas flow tube technique.

The pressure dependent emission spectra were obtained from a sample with a size of about $50 \,\mu m \times 50 \,\mu m$ $\times 50 \,\mu m$ enclosed in a homebuilt gasketed sapphire anvil cell.¹⁹ Berylco gaskets with a 300 μm diameter hole were used. Due to the slightly hygroscopic nature of the Cs₂NaScCl₆ material, Merck spectroscopic paraffin oil was used as the pressure transmitting medium instead of the more commonly used methanol–ethanol mixture. Calibration of



FIG. 2. Shift of the ${}^{4}T_{2g} \rightarrow {}^{4}A_{2g}$ emission band maxima as a function of hydrostatic pressure at 15 K (O) and 300 K (\Box).

the applied pressure occurred with the ruby R-line luminescence method.¹ Up to 44 kbar the ruby R-line luminescence showed no significant broadening, indicating that the pressure stayed hydrostatic. Cooling of the whole pressure cell occurred in an appropriate homebuilt He gas flow cryostat.¹⁹ The excitation source and the detection system for the sample luminescence was as described above. The ruby R-line luminescence was recorded with a RCA C31034 photomultiplier tube connected to a photon counting system (SR 400).

All luminescence spectra were corrected for the wavelength dependence of the sensitivity of the detection system and were converted to photon counts versus energy using the procedure described by Ejder.²⁰



FIG. 3. (a) Experimental 15 K ${}^{4}T_{2g} \rightarrow {}^{4}A_{2g}$ emission spectra of 4.1% Cr³⁺:Cs₂NaScCl₆ at various hydrostatic pressures. (b) Simulated emission band shapes based on Eqs. (6) and (7) and the parameters given in Table II.

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III. RESULTS

In the left part of Fig. 1 the 7 K ambient pressure ${}^{4}T_{2g}$ $\rightarrow {}^{4}A_{2g}$ luminescence spectrum of 4.1% Cr³⁺ doped Cs₂NaScCl₆ is shown. Vibrational progressions in two CrCl₆³⁻ local modes are observed, and they have previously been identified as a_{1g} and e_g normal modes.¹⁶ In the right part of Fig. 1 the 15 K ambient pressure absorption spectrum of 4.1% Cr³⁺:Cs₂NaScCl₆ in the spectral region of the ${}^{4}A_{2g} \rightarrow {}^{4}T_{2g}$ and ${}^{4}A_{2g} \rightarrow {}^{2}E_{g}$ transitions is shown.

Figure 2 displays the pressure dependence of the ${}^{4}T_{2g}$ $\rightarrow {}^{4}A_{2g}$ emission band maximum at 15 K (circles) and 300 K (squares). Upon increasing pressure the emission undergoes an overall blue shift of 19 cm⁻¹/kbar at 15 K and 28 cm⁻¹/kbar at 300 K, as emphasized by the solid lines in Fig. 2, which are linear regression fits to the experimental data.

In Fig. 3(a) the 15 K ${}^{4}T_{2g} \rightarrow {}^{4}A_{2g}$ luminescence spectra at ambient pressure, 11, 22, and 44 kbar (from top to bottom) are shown. Due to the small sample size and the geometry of the enclosing pressure cell used in this experiment, the detection limit of the sample emission was relatively high and the monochromator slits had to be opened. Thus the resolution of these spectra is instrumentally limited. Nevertheless, some vibrational fine structure is resolved. Note that upon increasing pressure there are remarkable and very significant intensity redistributions within this luminescence band.

IV. DISCUSSION

A. The $\operatorname{Cr}^{3+4}A_{2g} \leftrightarrow {}^{4}T_{2g}$ transitions at ambient pressure

In the $Cs_2NaScCl_6$ elpasolite host, Cr^{3+} is exactly octahedrally coordinated by six chloride anions. Chloride is a weak field ligand,²¹ and therefore, under ambient pressure conditions the ${}^{4}T_{2g}$ origin lies about 2400 cm⁻¹ below the ${}^{2}E_{o}$ origin, see Fig. 1. This fact enables us to study the effect of pressure on the pure ${}^{4}T_{2g} \rightarrow {}^{4}A_{2g}$ luminescence transition over a large pressure range, before the pressure induces a crossover in the emitting excited state from ${}^{4}T_{2g}$ to ${}^{2}E_{g}$. It has been demonstrated for Cr3+:Cs2NaYCl6 that first evidence of this crossover occurs at pressures above 83 kbar.²² This is in contrast to Cr³⁺ doped fluoride and oxide weakfield systems in which the ambient pressure ${}^{4}T_{2g} - {}^{2}E_{g}$ energy separation is typically on the order of a couple of hundred to about a thousand wave numbers. Even though oxides and fluorides are somewhat less compressible than the chlorides (see Sec. IVB), this typically leads to a significant amount of ${}^{2}E_{g} \rightarrow {}^{4}A_{2g}$ luminescence already at moderately low pressures of about 20-40 kbar.9,10

The 15 K ambient pressure ${}^{4}A_{2g} \leftrightarrow {}^{4}T_{2g}$ absorption and emission bands in Fig. 1 are almost mirror images. Differences, in particular the better resolution of the emission spectrum, are due to the splitting of the electronic ${}^{4}T_{2g}$ state in its four spinors Γ_7 , Γ_8 , Γ_8 , and Γ_6 , whereas the ${}^{4}A_{2g}$ ground state does not split. 16,23 Consequently, in the 15 K absorption spectrum we observe a superposition of four essentially unresolved absorption bands. In the 7 K emission spectrum this is not the case since only the lowest of the four ${}^{4}T_{2g}$ spinors has a significant population at this temperature.

TABLE I. Pressure induced band maximum energy shift rates of the Cr^{3+} ${}^{4}T_{2g} \rightarrow {}^{4}A_{2g}$ room temperature luminescence of various CrX_{6}^{n-} octahedral units in some selected host lattices.

Considered species	Host lattice	Shift rate [cm ⁻¹ /kbar]	M ³⁺ -X distance (Å)
${ m CrO_{6}^{9-}}\ { m CrF_{6}^{3-}}\ { m CrCl_{6}^{3-}}$	$\begin{array}{c} Gd_{3}Ga_{5}O_{12}\\ Na_{3}In_{2}Li_{3}F_{12}\\ Cs_{2}NaScCl_{6} \end{array}$	10 ^a 15 ^b 28 ^c	≈1.9 ≈1.9 ≈2.5

^aFrom Ref. 10.

^bFrom Ref. 31.

^cThis work.

The ${}^{4}A_{2g} \leftrightarrow {}^{4}T_{2g}$ transition is magnetic dipole (MD) allowed and electric dipole (ED) forbidden. It has been shown that its main intensity derives from a vibronically induced ED-mechanism. The t_{2u} and t_{1u} normal modes of the CrCl_6^{3-} octahedral unit have been identified as the dominant enabling modes.^{16,24} On each of these as well as on the weaker MD-origin(s), vibrational progressions in the a_{1g} and e_g modes are built. These progressions reflect a distortion of the ${}^{4}T_{2g}$ state along the $Q_{a_{1g}}$ and Q_{e_g} nuclear coordinates relative to the ${}^{4}A_{2g}$ ground state, i.e., a totally symmetric and a Jahn–Teller distortion.²⁵ The orbital degeneracy of the ${}^{4}T_{2g}$ state is responsible for the occurrence of a Jahn–Teller effect in this electronic state.^{26,27} Previous ambient pressure studies on the Jahn–Teller effect in the $\text{Cr}^{3+4}T_{2g}$ state in various host matrices show that this is a pure T \otimes e Jahn–Teller case.^{14-16,23,24}

B. Pressure effect on the ${}^{4}T_{2g} \rightarrow {}^{4}A_{2g}$ emission band maximum: Estimate of the compressibility of the CrCl₆³⁻ unit with the point charge model

The ${}^{4}T_{2g} \rightarrow {}^{4}A_{2g}$ luminescence transition involves an electron promotion from the strongly antibonding e_{g} -set of d-orbitals to the weaker antibonding t_{2g} -set, and it is thus a measure of the octahedral ligand field parameter 10Dq at the equilibrium geometry of the emitting state. Pressure decreases the $Cr^{3+}-Cl^{-}$ distances and thus increases 10Dq. Consequently, the ${}^{4}T_{2g} \rightarrow {}^{4}A_{2g}$ emission band maximum is expected to undergo a blue shift upon increasing pressure.28 This is exactly what we observe experimentally (see Fig. 2): In the 1 bar–50 kbar pressure range the emission band maximum undergoes a linear blue shift with rates of 19 and 28 $cm^{-1}/kbar$ at 15 K and room temperature, respectively. For our simple analysis we neglect the pressure dependence of the vibrational frequencies involved and assume linear coupling, i.e., the same frequencies in the ground and excited states. This has been proved reasonable for other systems.²⁹

The linear regression fits in Fig. 2 clearly show that the pressure dependence of the emission band maximum is far stronger at room temperature than at 15 K. First we have to consider the following effect: In contrast to 15 K, at 300 K there is a significant population of the t_{2u} and t_{1u} vibronic levels of ${}^{4}T_{2g}$. Therefore, at 300 K, there is a contribution to the observed blue shift from the pressure dependence of the t_{2u} and t_{1u} vibrational energies in ${}^{4}T_{2g}$. Assuming a pressure induced shift rate of 0.5 cm⁻¹/kbar for the t_{2u} and t_{1u} vibrational energies, ²² and taking the 300 K Boltzmann population of these t_{2u} and t_{1u} vibronic ${}^{4}T_{2g}$ levels into account, we

estimate that this effect only accounts for 10% of the increase in the shift rate between 15 and 300 K.

We conclude that the compressibility of the CrCl_6^{3-} unit in the electronic ${}^4T_{2g}$ state at the two temperatures is significantly different. Two factors determine the compressibility of CrCl_6^{3-} in this lattice: The compressibility of the $\text{Cs}_2\text{NaScCl}_6$ crystal itself, i.e., a bulk property of the host material. The second is the local compressibility of the CrCl_6^{3-} unit. Both these compressibilities decrease with decreasing temperature, but not necessarily with the same rate. The decreasing compressibilities are a result of the decreasing inter-ionic distances with decreasing temperature. And these are usually attributed to anharmonicities in the inter-atomic potentials. In NaCl a lattice contraction of 0.1% between room temperature and 4.2 K has been reported.³⁰

It is interesting to compare the pressure dependence of the $Cr^{3+4}T_{2g} \rightarrow {}^{4}A_{2g}$ emission energy in $Cr^{3+}:Cs_2NaScCl_6$ with Cr^{3+} doped oxides and fluorides. Table I shows that in $Cr^{3+}:Gd_3Ga_5O_{12}$ and $Cr^{3+}:Na_3In_2Li_3F_{12}$ at room temperature this emission undergoes a pressure induced blue shift of 10 and 15 cm⁻¹/kbar, respectively, compared to 28 cm⁻¹/kbar in the title compound.^{10,31} The increasing shift rate along the series oxide<fluoride<chloride reflects two facts: First, the bulk compressibility increases along this series of materials. This trend is continued to the heavier halides, and it is well documented for example along the series NaF, NaCl, NaBr, NaI.³² Second, the $Cr^{3+}-X^{n-}$ distances also increase along the series oxide≈fluoride<chloride (see Table I), and this is known to increase the local compressibility.³³

Based on the data in Fig. 2 we now attempt to estimate the effective compressibility χ of the CrCl_6^{3-} unit in $\text{Cs}_2\text{NaScCl}_6$ from the pressure dependent emission band maxima. This is a commonly used procedure to estimate χ in transition metal complexes.^{13,34} For this purpose we use the traditional point charge model,²⁸ and thus we neglect the ${}^4T_{2g}$ Jahn–Teller distortion for the moment. Approximating the Cl⁻ ligands as point charges, the octahedral ligand field parameter Dq can be expressed as²⁸

$$Dq = \frac{Z \cdot e^2 \cdot \langle r^4 \rangle_{3d}}{6 \cdot R^5},\tag{1}$$

i.e., Dq is proportional to R^{-5} , where R represents the metal (Cr^{3+}) -ligand (Cl^{-}) distance. A dependence close to R^{5} has been obtained theoretically for CrF_{6}^{3-} in fluoroelpasolites using a Molecular Orbital description.³⁵ Since we are considering ${}^{4}T_{2g}$ emission, we are dealing with Dq of the relaxed ${}^{4}T_{2g}$ excited state. From Eq. (1) it follows that Dq is proportional to $V^{-5/3}$, where V is the volume of the octahedral $CrCl_{6}^{3-}$ unit, and consequently we obtain³⁶

$$\ln\left(\frac{Dq}{Dq_0}\right) = -\frac{5}{3} \cdot \ln\left(\frac{V}{V_0}\right) + \text{constant},$$
(2)

where the zero subscript denotes ambient pressure quantities. The definition of the compressibility χ is as follows:³³

From Eqs. (2) and (3) the following relation between χ and Dq is obtained:

$$\chi = \frac{3}{5} \cdot \frac{d \ln\left(\frac{Dq}{Dq_0}\right)}{dP}.$$
(4)

A plot of the experimental $\ln(Dq/Dq_0)$ values versus pressure *P* (not shown) and a linear regression fit to these data yields $\chi = 9.7 \cdot 10^{-4} \text{ kbar}^{-1}$ for the 15 K and $\chi = 1.47 \cdot 10^{-3} \text{ kbar}^{-1}$ for the room temperature compressibility. These values can now be used to estimate the decrease of the $\text{Cr}^{3+}-\text{Cl}^{-}$ equilibrium distance as a function of pressure. The relative decrease of metal–ligand bond lengths $\Delta R/R$ is related to the compressibility by³⁷

$$\frac{\Delta R}{R} = -\frac{\chi}{3} \cdot P. \tag{5}$$

With P = 44 kbar and R = 2.5 Å,¹⁶ we obtain $\Delta R = -0.036$ Å(15 K) and $\Delta R = -0.054$ Å(300 K), i.e., a reduction of the Cr³⁺ – Cl⁻ equilibrium distance by 0.036 Å/0.054 Å at 44 kbar.

C. Intensity redistributions in the ${}^{4}T_{2g} \rightarrow {}^{4}A_{2g}$ emission band with pressure: Effect on force constants and Huang–Rhys parameters

In the previous section we have only considered the band maximum energy shift of the ${}^{4}T_{2g} \rightarrow {}^{4}A_{2g}$ luminescence band. The experimental data in Fig. 3(a) show that in addition to the blue shift of the whole emission band upon increasing pressure, there are significant intensity redistributions within this luminescence band. A profound analysis of the emission band shape as a function of pressure is the aim of this Section. As mentioned in Sec. III, the resolution of the spectra in Fig. 3(a) is instrumentally limited. This becomes obvious after comparison of the top spectrum in Fig. 3(a)with Fig. 1. Thus, what in the pressure dependent spectra appears at first sight as a regular progression in one normal mode, is in reality the result of a superposition of a vibrational coupling of the ${}^{4}T_{2g} \rightarrow {}^{4}A_{2g}$ transition to two normal modes, namely a_{1g} and $e_g^{z_s}$ built on several vibronic origins, see Sec. IV A. This is why none of the spectra in Fig. 3(a) can be modeled within a harmonic single configurational coordinate (SCC) picture.³⁸

In order to quantify the simultaneous a_{1g} and e_g distortions, we use Heller's time-dependent theory of electronic spectroscopy.^{39,40} This approach is superior to a Franck–Condon analysis as soon as multiple distortions between two electronic states occur. It calculates the temporal evolution of the initial state eigenfunction on the final state, and this is mathematically described by the so-called autocorrelation function³⁸

$$\langle \phi | \phi(t) \rangle = \exp \left\{ \sum_{k} \left[-S_{k} \cdot (1 - \exp(-i \cdot \omega \cdot t)) - \frac{i \cdot \omega_{k} \cdot t}{2} \right] - i \cdot E_{0} \cdot t - \Lambda^{2} \cdot t^{2} \right\},$$
(6)

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TABLE II. Summary of the parameters used to calculate the spectra shown in Fig. 3(b): Vibrational energies $h \cdot \nu$ of the a_{1g} and e_g modes of the octahedral $\operatorname{CrCl}_6^{3-}$ unit and the respective force constants *f*, Huang–Rhys parameters *S*, energy of the zero-phonon transition E_0 and damping factor Λ [see Eq. (6)] as a function of pressure.

P/kbar	$h \cdot \nu_{a_{1g}}/\mathrm{cm}^{-1}$	$h \cdot \nu_{e_g} / \mathrm{cm}^{-1}$	$f_{a_{1g}}\left[\mathrm{N/m}\right]$	$f_{e_g} \left[\mathrm{N/m} \right]$	$S_{a_{1g}}$	S_{e_g}	$E_0 / { m cm}^{-1}$	Λ/cm^{-1}
0.001	298	236	185.7	116.5	1.411	1.445	11 974	40
11	303	241	192.0	121.5	1.345	1.353	12 158	42.5
22	311	249	202.3	129.5	1.240	1.264	12 308	45
44	322	260	216.9	191.4	1.095	1.115	12 745	52.5

where S_k is the Huang–Rhys parameter for the normal coordinate k and E_0 is the energy of the zero-phonon transition. Λ is a damping factor which determines the width of the individual vibrational lines, and its physical meaning is a relaxation into other modes or into the thermal bath.⁴¹ The emission spectrum is the Fourier transform of the time domain function

$$I(\omega) = C \cdot \omega^3 \cdot \int_{-\infty}^{\infty} \exp(i \cdot \omega \cdot t) \cdot \langle \phi | \phi(t) \rangle \cdot dt, \qquad (7)$$

where $I(\omega)$ is the intensity in photons emitted per unit time at frequency ω . *C* is a constant. We have previously used this approach to model the 7 K⁴T_{2g} \rightarrow ⁴A_{2g} emission spectrum in Fig. 1.¹⁶ The a_{1g} and e_g progressions built on four different origins were calculated: the MD allowed $\Gamma_7({}^4T_{2g})$ \rightarrow $\Gamma_8({}^4A_{2g})$ origin, and the ED vibronic origins induced by the t_{2u} , t_{1u} as well as the t'_{1u} modes of the CrCl_6^{3-} unit. Their relative contributions to the total emission intensity were 1:8.2:9.5:5.3, respectively. The ambient pressure CrCl_6^{3-} vibrational a_{1g} and e_g energies are 298 and 236 cm⁻¹, respectively. Using the above ratios and vibrational energies we calculated emission band shapes using Eqs. (6) and (7). The best fit to the experimental spectrum in Fig. 1 was obtained with the parameters $E_0 = 11974 \text{ cm}^{-1}$, $S_{a_{1g}} = 1.411$, S_{e_g} = 1.445, and $\Lambda = 16 \text{ cm}^{-1}$.¹⁶

We used the same parameters to simulate the less well resolved ambient pressure spectrum in Fig. 3(a) (top trace), except for Λ , for which a value of 40 cm⁻¹ accounts for the instrumental broadening. Thus Λ loses its original physical significance here. The result of this calculation is shown in the top trace of Fig. 3(b). The agreement with the experimental spectrum, in particular regarding the intensity distribution, is very good as expected.

The same set of parameters was then used as starting values for fits with Eqs. (6) and (7) to the experimental 11, 22, and 44 kbar spectra in Fig. 3(a). In order to avoid overparametrization, we made the following assumptions: First, we neglect the vibrational side bands on the Γ_7 MD-origin since they account for less than 5% of the total intensity (see above), and secondly we assume that the energies of the t_{2u} , t_{1u} , and t_{1u} modes have identical pressure dependences. Pressure dependent data on vibrational energies of u-modes are scarce. Reference 22 shows that the t_{2u} and t_{1u} vibrational energies of CrCl_6^{3-} in $\text{Cr}^{3+}:\text{Cs}_2\text{NaYCl}_6$ increase with 0.3 and 0.8 cm⁻¹/kbar. Up to a pressure of 44 kbar this will only lead to offsets of about 20 cm⁻¹ between individual false origins. This lies well within the resolution limit of our experimental spectra, and therefore, our assumption is reasonable. We further assume that the intensity ratios between the individual false origins and their associated vibrational side bands do not change in the 1 bar–44 kbar pressure range. This is justified by the fact that these ratios do not change significantly between the spectra of CrCl_6^{3-} in various chloride elpasolite host lattices in which the chemical pressure on the Cr^{3+} dopant ion is significantly different.^{15,16,23} Finally, we assume that the pressure induced shift of the a_{1g} and e_g vibrational energies is identical. The pressure dependent Raman data from $\text{Cr}^{3+}:\text{Cs}_2\text{NaYCl}_6$ and $\text{Cr}^{3+}:\text{K}_2\text{NaScF}_6$ presented in Ref. 42 demonstrate that this also is a reasonable assumption.

For the actual fit procedure we thus have five independent fit parameters: $\Lambda, E_0, S_{a_{1g}}, S_{e_g}, \Delta \nu$ [where $\nu_{a_{1g}}(P) = \nu_{a_{1g},P=0} + \Delta \nu \cdot P$ and $\nu_{e_g}(P) = \nu_{e_g,P=0} + \Delta \nu \cdot P$]. In this section we are interested in the latter three. Since we have well defined starting values for all these parameters, i.e., their ambient pressure values, such a five-parameter fit for the 11, 22, and 44 kbar spectra in Fig. 3(a) is reasonable in view of their resolved fine structure. The results of these fits are shown in Fig. 3(b), and their agreement with experiment is generally very good. Both the energy shifts and the change in the intensity distribution are nicely reproduced. All fit parameters are summarized in Table II.

The vibrational energies of the a_{1g} and e_g modes in-



FIG. 4. Pressure dependence of the vibrational energies of the a_{1g} (\bigcirc) and e_g (\square) normal modes of the CrCl₆³⁻ unit in Cs₂NaScCl₆. These data were extracted from fits with Eqs. (6) and (7) to the pressure dependent 15 K ${}^{4}T_{2g} \rightarrow {}^{4}A_{2g}$ emission spectra in Fig. 3(a). The lines are linear regression fits to these data with slopes of 0.55 cm⁻¹/kbar.

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TABLE III. Changes of the equilibrium geometry of the $CrCl_6^{3-}$ unit in the ${}^{4}T_{2g}$ first excited state relative to the ${}^{4}A_{2g}$ ground state as a function of external pressure. $Q_{a_{1g}}$ and Q_{e_g} are normal coordinates. x_{eq} , y_{eq} , z_{eq} are $Cr^{3+}-Cl^{-}$ equilibrium distances in the ${}^{4}T_{2g}\xi$ excited state relative to the ${}^{4}A_{2g}$ ground state. The pressure dependence of the Jahn–Teller energy E_{JT} is given in the last column.

<i>P</i> /kbar	${\Delta Q_{a_{1g}}}_{({ m \AA})}^{a_{1g}}$	$\Delta Q_{e_g \mathrm{eq}} \ (\mathrm{\AA})$	$\Delta x_{ m eq}, \Delta y_{ m eq}$ (Å)	$\Delta_{\mathcal{Z}_{eq}}$ (Å)	$E_{\rm JT}/{\rm cm}^{-1}$
0.001	0.095	-0.108	0.070^{a}	-0.024^{a}	341
11	0.092	-0.103	0.067	-0.022	326
22	0.087	-0.098	0.064	-0.021	315
44	0.080	-0.090	0.059	-0.019	290

^aDifferences to the values in Ref. 16 are due to a calculation error in the respective reference.

crease linearly up to 44 kbar with 0.55 $\text{cm}^{-1}/\text{kbar}$. This is illustrated by the linear regression fits to the $\nu_{a_{1g}}, \nu_{e_g}$ data in Fig. 4. The increase of vibrational energies at higher pressures is usually explained with the increase of the force constant f of a given potential energy surface as the metalligand distance gets shorter. Our $\nu_{a_{1g}}, \nu_{e_g}$ shift rate of 0.55 cm⁻¹/kbar for CrCl₆³⁻ in Cs₂NaScCl₆ compares to shift rates of 1.1/1.2 cm⁻¹/kbar for these modes in Cr³⁺:Cs₂NaYCl₆.²² The bulk compressibility of the Cs₂NaScCl₆ and Cs₂NaYCl₆ materials is unknown. However, since these are both isostructural chloride materials, their compressibility is assumed to be very similar. We attribute the factor of 2 difference to a difference in the local compressibility of the $CrCl_6^{3-}$ unit in these two host matrices. It has been demonstrated for ruby that in cases where the dopant ion is larger than the host ion it substitutes, the local compressibility at the impurity site is lower than in the bulk of the host.^{43,44} For the other situation of a smaller dopant than host ion, we therefore expect a higher local compressibility of the impurity site than bulk compressibility. From the ionic radii of $Cr^{3+}(0.615 \text{ Å}), Sc^{3+}(0.745 \text{ Å}), \text{ and } Y^{3+}(0.900 \text{ Å}),^{45} \text{ we}$ thus expect a higher local $CrCl_6^{3-}$ compressibility and a stronger pressure dependence of the vibrational energies in Cr³⁺:Cs₂NaYCl₆ than in Cr³⁺:Cs₂NaScCl₆. The reduction of S for both a_{1g} and e_g modes with increasing pressure (Table II) is a manifestation of the fact that pressure reduces the expansion of the CrCl_6^{3-} unit upon photo-excitation from ${}^{4}A_{2g}$ to ${}^{4}T_{2g}$, and this will now be quantified. An insight into the microscopic origin of the S-dependence upon R is given in Ref. 35.

D. The equilibrium geometry of the $CrCl_6^{3-}$ complex in the ${}^{4}T_{2g}$ excited state as a function of hydrostatic pressure

In a simple linear harmonic coupling picture, the Huang–Rhys parameter characterizes the relative displacement ΔQ of two potentials³⁸

$$S_k = \frac{f_k \cdot \Delta Q_k^2}{2 \cdot h \cdot \nu_k}.$$
(8)

This picture assumes harmonic initial and final state potentials, as well as identical force constants f for the two potentials. Using the FG matrix method in Ref. 46 the force con-



FIG. 5. Single configurational coordinate (SCC) diagrams showing the ${}^{4}T_{2g}$ excited-state potentials at ambient pressure and 44 kbar for (a) the a_{1g} and (b) the e_{g} normal coordinate. The zero points for the two coordinates correspond to the ${}^{4}A_{2g}$ ground-state potential minimum.

stants $f_{a_{1g}}$ and f_{e_g} can be calculated. Input data are the vibrational a_{1g} and e_g energies for the various applied pressures in Table II. At ambient pressure these force constants are $f_{a_{1g}} = 185.7$ N/m and $f_{e_g} = 116.5$ N/m, see Table II. Up to 44 kbar they increase by 17% and 21%, respectively, indicating that the e_g force constant is more susceptible to pressure than a_{1g} . The absolute equilibrium displacements $|\Delta Q_k|_{eq}$ of the electronic ${}^4T_{2g}$ state relative to ${}^4A_{2g}$ along the a_{1g} and e_g coordinates can now be calculated with Eq. (8). As shown in Table III, we obtain $|\Delta Q_{a_{1g}}|_{eq} = 0.095$ Å and $|\Delta Q_{e_g}|_{eq} = 0.108$ Å for ambient pressure, and up to 44 kbar these values are reduced to 0.080 and 0.090 Å, respectively. Based on group theoretical considerations and the ${}^4T_{2g}$ wave functions, it has been demonstrated that the sign of $\Delta Q_{a_{1g}}$ is positive, whereas the sign of ΔQ_{e_g} is negative. 14,47,48 We



FIG. 6. (a) Equatorial $(\Delta x, \Delta y)$ and axial (Δz) equilibrium distortions of the CrCl₆³⁻ unit in the ${}^{4}T_{2g}$ first excited state relative to the ${}^{4}A_{2g}$ ground state in Cr³⁺:Cs₂NaScCl₆ as a function of hydrostatic pressure at 15 K. (b) Pressure-dependence of the Jahn–Teller stabilization energy in Cr³⁺:Cs₂NaScCl₆.

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summarize the effect of pressure on the a_{1g} and e_g potentials in ${}^{4}T_{2g}$ relative to ${}^{4}A_{2g}$ in the simple SCC diagrams of Fig. 5.

For the further treatment of this Jahn–Teller problem it is sufficient to consider one single orbital component of the electronic ${}^{4}T_{2g}$ state, i.e., for example ${}^{4}T_{2g}\xi$.^{14,47} Although each of the three orbital ${}^{4}T_{2g}$ partners (ξ, η, ζ) distorts along a different direction in $Q_{e_g\theta}, Q_{e_g\epsilon}$ -space, this approach is feasible because these distortions are related by symmetry and are simply $Q_{e_g\theta}$ distortions. Thus we can convert the $\Delta Q_{a_{1g},eq}/\Delta Q_{e_g,eq}$ values to internal coordinates, i.e., metal– ligand equilibrium distance changes using the following transformation:¹⁴

$$\begin{pmatrix} \Delta x \\ \Delta y \\ \Delta z \end{pmatrix} = \begin{pmatrix} \frac{1}{\sqrt{6}} & 0 & \frac{1}{\sqrt{3}} \\ \frac{1}{\sqrt{6}} & \frac{1}{2} & -\frac{\sqrt{3}}{6} \\ \frac{1}{\sqrt{6}} & \frac{1}{2} & -\frac{\sqrt{3}}{6} \end{pmatrix} \cdot \begin{pmatrix} \Delta Q_{a_{1g}} \\ \Delta Q_{e_{g\theta}} \\ \Delta Q_{e_{g\epsilon}} \end{pmatrix}.$$
(9)

The $\Delta x_{eq} = \Delta y_{eq}$ and Δz_{eq} values obtained in this manner are listed in Table III. They indicate that the combined effect of the a_{1g} and e_{g} displacements is a net equatorial expansion and a smaller axial contraction. The pressure dependence of these values is illustrated in Fig. 6(a) and the values are listed in Table III. The equatorial expansion reduces with $2.5 \cdot 10^{-4}$ Å/kbar upon increasing pressure. The axial compression reduces also, but only with $1.1 \cdot 10^{-4}$ Å/kbar. Thus the net effect of hydrostatic pressure on the $CrCl_6^{3-}$ equilibrium geometry in the electronic ${}^{4}T_{2g}$ state is a reduction of the tetragonal distortion, corresponding to a partial quenching of the Jahn-Teller (JT) effect. This is also reflected in the pressure dependent Jahn-Teller stabilization energies $E_{\rm TT}$ given in the last column of Table III. Since we are dealing with a Jahn-Teller distortion exclusively along the e_g coordinate, $E_{\rm JT}$ can be calculated as follows:

$$E_{\rm JT} = h \cdot \nu_{e_a} \cdot S_{e_a}.\tag{10}$$

Our ambient pressure $E_{\rm JT}$ value here, obtained from an analysis of the vibrational luminescence fine structure, differs from the $E_{\rm JT}$ value for ${\rm CrCl}_6^{3-}$ in Cs₂NaScCl₆ obtained from an analysis of the Ham effect by about 13%.^{16,49} Considering the fact that these are values obtained from different data sets this agreement is reasonable.

Figure 6(b) shows that in the 1 bar–44 kbar pressure range $E_{\rm JT}$ decreases linearly with a rate of $-1.1 {\rm ~cm^{-1}/kbar}$. This is in line with previous (ambient pressure) studies of the Jahn–Teller effect in ${\rm CrCl}_6^{3-}$ doped into the chemically slightly different host lattices ${\rm Cs}_2{\rm NaYCl}_6$, ${\rm Cs}_2{\rm NaInCl}_6$, and ${\rm Cs}_2{\rm NaScCl}_6$. 15,16,23 The ionic radii of the trivalent host ions, for which the ${\rm Cr}^{3+}$ dopant ion substitutes, decreases along the series ${\rm Y}^{3+}(0.900 {\rm ~\AA}) > {\rm In}^{3+}(0.800 {\rm ~\AA}) > {\rm Sc}^{3+}(0.745 {\rm ~\AA})$. ⁴⁵ Thus the ${\rm CrCl}_6^{3-}$ unit experiences an increasing pressure along the series ${\rm Cr}^{3+}:{\rm Cs}_2{\rm NaYCl}_6 < {\rm Cr}^{3+}:{\rm Cs}_2{\rm NaInCl}_6$ $<{\rm Cr}^{3+}:{\rm Cs}_2{\rm NaScCl}_6$. It was found that this is accompanied by a decreasing Jahn–Teller stabilization energy.¹⁶ Figure 5 shows that for both the a_{1g} and e_g mode the dominant pressure effect is a vertical displacement of the excited-state potential to higher energy. This is with respect to the ground state potential, the minimum of which defines the origin of the coordinate systems in Fig. 5 at both pressures. The main effect of pressure is thus an increase of the vertical ${}^4T_{2g} - {}^4A_{2g}$ energy difference, and this is why the simple analysis based on the emission maximum (Sec. IV B) represents a reasonable approximation.

V. CONCLUSIONS

By analyzing the position and vibrational fine structure of $\operatorname{Cr}^{3+4}T_{2g} \rightarrow {}^{4}A_{2g}$ luminescence at 15 K as a function of hydrostatic pressure, we have shown that the Jahn-Teller distortion in the electronic ${}^{4}T_{2g}$ state of $CrCl_{6}^{3-}$ is reduced with increasing pressure. Our study of CrCl₆³⁻ in Cs₂NaScCl₆ represents the first case where this has been studied experimentally. Further, we have demonstrated that the effect of pressure is larger for the $Cr^{3+4}T_{2g}$ state than for the ${}^{4}A_{2g}$ state, in particular also regarding distortions along the totally symmetric a_{1g} coordinate. The observation of vibrational fine structure is imperative for the type of analysis we have applied. In the vast majority of transition metal ion system which have been studied with high-pressure techniques so far, such ligand field dependent luminescence or absorption transitions as observed here did not reveal any vibrational fine structure. In these cases the analysis of the effect of pressure on the excited state distortions is often restricted to a simple point charge model, which only uses the pressure induced shifts of the band maxima as input data. Many of these pressure studies involve luminescence transitions originating from an excited state which is Jahn-Teller susceptible. Examples are Ti³⁺, ³⁶ V³⁺, ⁵⁰ Cr³⁺, ^{22,51} Mn²⁺, ⁵¹⁻⁵³ Co²⁺, ^{36,54} and Ni²⁺. ^{36,54,55} Our study demonstrates that up to pressures of 44 kbar for $CrCl_6^{3-}$ in $Cs_2NaScCl_6$, the pressure induced changes of the ${}^{4}T_{2g}$ geometry relative to ${}^{4}A_{2g}$ are small compared to the *absolute* distortions of ${}^{4}T_{2g}$ relative to ${}^{4}A_{2g}$. This shows that the basic assumptions of the simple point charge model are reasonable for determining pressureinduced metal-ligand distance changes. But it is clear that the more sophisticated treatment based on the intensity distribution and using two coordinates provides more fundamental and more detailed insight into the excited-state properties.

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