High-pressure induced absorption line narrowing in 
$\text{Cs}_3\text{Yb}_2\text{Cl}_9$

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Abstract. In this paper we investigate the pressure dependence of the absorption spectrum of $\text{Cs}_3\text{Yb}_2\text{Cl}_9$. The polarised absorption spectra enable us to assign the main transitions of Yb$^{3+}$ in $C_{3v}$ from the complicated phonon-side band structure, and derive the corresponding structure. Special attention is paid on the pressure-induced line narrowing and associated blue shift of the most prominent absorption transition that corresponds to the high energy $\Gamma_4 \rightarrow \Gamma_4$ transition at 10668 cm$^{-1}$ at ambient conditions. The unusual linewidth reduction with pressure is explained by a Debye-type model considering the different contributions to the linewidth.

1. Introduction
Within the lanthanides the Yb$^{3+}$ ion (4f$^{13}$) has one of the simplest energy level schemes: it has only one f-f excited state $^2F_{5/2}$ at around 10000 cm$^{-1}$ above the ground state $^2F_{7/2}$. The number of Stark sublevels depends on the crystal field environment. However, in spite of this simplicity, Yb$^{3+}$ is the most intriguing of all lanthanides: broad lines, strong electron-phonon coupling strength, laser action, and most unusual optical bistability effect have been found in Yb$^{3+}$-based compounds. The first two phenomena are related to the interaction with neighboring ions. The optical bistability behavior is still open, and it was at first interpreted as a result of the coupling between two Yb ions [1]. Later, a careful experimental work led to a different explanation [2]. An electronic origin increases its oscillator strength upon increasing temperature, leading to a feedback effect: the stronger the absorption the
more the crystal heats up leading to a stronger absorption and so on. In any case, the environment of Yb$^{3+}$ plays a fundamental role in all spectroscopic properties.

The use of high hydrostatic pressure is the best technique for modifying the bond distances around the Yb$^{3+}$ ions in a given crystal. In particular, pressure modifies the crystal-field strength and, consequently, the splitting and oscillator strength of transitions between $^3F_{7/2}$ and $^3F_{5/2}$ sublevels.

We report on the influence of hydrostatic pressure on the spectroscopic properties of Cs$_3$Yb$_2$Cl$_9$. The crystal structure consists of Yb$_2$Cl$_9^{3-}$ dimer units of two face sharing YbCl$_6^{3-}$ octahedra. The single-ion symmetry is C$_3v$ whereas the dimer is axially distorted with D$_3$ symmetry (approximate D$_{3h}$) with the three-fold axis parallel to the crystal c axis [3]. The Yb-Yb distance is the closest possible in a chloride lattice.

2. Experimental

Single crystals of Cs$_3$Yb$_2$Cl$_9$ were grown in silica ampoules using the Bridgman technique [4]. It crystallizes in the trigonal space group R$ar{3}$c [3]. Polarized and unpolarised temperature dependent absorption spectra at ambient pressure were measured with a Cary 6000i in the 6-300 K temperature range using a closed-cycle cryostat. Pressure dependent absorption spectra were obtained in a diamond anvil cell (DAC) with a homemade setup with non-oriented microsamples and unpolarised light. The procedure is as follows: the modulated light (chopped with a frequency controller SR-540) of a tungsten lamp is focused on the sample with a microscope objective. The transmitted light is collected with another microscope objective and dispersed by a 0.5 m monochromator (Chromex 500IS) and detected synchronously (lock-in SR-830) by a thermoelectrically cooled InGaAs detector (Electro Optical Systems, Inc.). Hydrostatic pressure experiments were performed in a membrane DAC with silicon oil as pressure transmitter. The ruby fluorescence was used for pressure calibration.

3. Results and Analysis

Figure 1 shows the polarized temperature-dependent absorption spectra of Cs$_3$Yb$_2$Cl$_9$ for E//c and E$\perp$c.

![Absorption spectra](image-url)

Fig. 1. Polarized optical absorption spectra of Cs$_3$Yb$_2$Cl$_9$ at different temperatures
These spectra allow us to identify the hot bands, vibronic sidebands as well as the electronic origins on the basis of transitions within the single-ion energy levels ($C_{3v}$ symmetry), as it is shown in Fig. 2. The crystal-field levels were determined from the absorption and emission spectra. According to double-group theory, the $^2F_{5/2}$ ground state splits into 5 levels $\Gamma_4$, $\Gamma_5$ and $\Gamma_6$, whereas the excited state splits into 4 levels $2\Gamma_4$, $\Gamma_5$ and $\Gamma_6$. The arrows indicate the electric-dipole allowed transitions for absorption. Their selection rules under $C_{3v}$ point symmetry allow $\Gamma_4 \rightarrow \Gamma_4$ in $\pi$ and $\sigma$ polarization, $\Gamma_4 \rightarrow \Gamma_5$, $\Gamma_6$ in $\sigma$ and $\Gamma_6 \rightarrow \Gamma_5$ and $\Gamma_5 \rightarrow \Gamma_6$ in $\pi$. From the 6 K absorption spectrum the electronic origins at 10193 cm$^{-1}$, 10241 cm$^{-1}$, 10460 cm$^{-1}$ and 10668 cm$^{-1}$ are assigned to $\Gamma_4 \rightarrow \Gamma_4$, $\Gamma_5$, $\Gamma_6$, $\Gamma_4$ transitions, respectively.

![Energy levels diagram for Yb$^{3+}$ in octahedral and trigonal symmetry.](image)

Fig. 2. Energy levels diagram for Yb$^{3+}$ in octahedral and trigonal symmetry.

![Pressure dependence of the unpolarized room temperature optical absorption spectra of Cs$_3$Yb$_2$Cl$_9$.](image)

Fig. 3 Pressure dependence of the unpolarized room temperature optical absorption spectra of Cs$_3$Yb$_2$Cl$_9$. 
In figure 3 we plot the room temperature absorption spectra of Cs$_3$Yb$_2$Cl$_9$ upon increasing pressure. Figures 4a and 4b show the line-shift and the line-width reduction, respectively, of the most prominent $\Gamma_4 \rightarrow \Gamma_4$ absorption peak with pressure. The peak is linearly blue-shifted from 10668 cm$^{-1}$ at ambient pressure to 10782 cm$^{-1}$ at 120 kbar at a rate of 0.73 cm$^{-1}$·kbar$^{-1}$. The shift is accompanied by a line narrowing from 63 cm$^{-1}$ to 40 cm$^{-1}$ ($\sim$ −0.2 cm$^{-1}$ kbar$^{-1}$), between ambient pressure and 120 kbar. As far as we know, this is the first report of such a pressure-induced line-width reduction. The effect is similar to that observed upon cooling at ambient pressure, but in such case, rather than bluenshift, a thermal redshift following a cotangent law is observed (Fig. 1). The pressure-induced line narrowing must be due to a reduction of the electron-phonon coupling strength with pressure.

The total linewidth, $H$, depends on temperature and pressure and involves contributions from zero-phonon line dispersion and Raman processes \cite{5, 6}. Within a Debye-type model, the homogeneous peak width is given by:

$$H(T) = \alpha \left( \frac{T}{T_D} \right)^7 \int_0^{T/T_D} \frac{x^6 e^x}{(e^x - 1)^2} \, dx$$  \hspace{1cm} (1)$$

where $x = \hbar \omega / kT$, $\alpha$ is the electron-phonon coupling parameter and $T_D = \hbar \omega_D / k$ is the Debye temperature. Taking into account the effective Grüneisen parameter for the Debye frequency, $\gamma = -\frac{d \ln \omega_D}{d \ln V}$, then $\frac{\partial T_D}{\partial P}$ is always positive provided that $\gamma > 0$, the same is true for $\frac{\partial H}{\partial \alpha}$. At constant temperature, the line-width, $H$, depends on pressure $P$ as follows:

$$\frac{dH}{dP} = \left( \frac{\partial H}{\partial \alpha} \right)_{T_0} \frac{\partial \alpha}{\partial P} + \left( \frac{\partial H}{\partial T_D} \right)_{\alpha} \frac{\partial T_D}{\partial P}$$  \hspace{1cm} (2)$$

The line-width reduction of Fig. 4b can be understood within this model since the second factor of Eq.2 is dominant given that $\frac{\partial H}{\partial T_D}$ is always negative and the Raman process becomes dominant at room temperature. If we assume that $\alpha$ scales with pressure as the Debye frequency does \cite{6}, then the
variation of the line-width is given by: \[ \frac{dH}{dP} = H \left( \frac{1}{\alpha} \frac{\partial \alpha}{\partial P} - 7 \frac{\gamma}{B_0} \right) \approx -6 \frac{\gamma}{B_0} H, \] where \( B_0 \) is the crystal bulk modulus. Taking typical values of \( \gamma = 1 \), \( B_0 = 300 \) kbar, and \( H = 60 \) cm\(^{-1}\), we find that \( \frac{dH}{dP} \approx -1 \) cm\(^{-1}\) kbar\(^{-1}\). This estimation is in fair agreement with the experimental results (Fig. 4b) taking into account that the pressure-induced narrowing is an underestimation of the actual homogenous narrowing since contributions from inhomogeneous broadening under pressure have not been considered in this model.

We are in the process of systematically studying the line narrowing phenomenon in other Yb\(^{3+}\)-based materials.

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