LUMINESCENCE OF $K_2Pt(SCN)_4$ SINGLE CRYSTALS AT HIGH PRESSURE

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Single-crystal emission spectra of $K_2Pt(SCN)_4$ have been measured at $T = 100$ K under high pressures up to 57 kbar The observed blue-shift of ≈ 10 cm^{-1}/kbar can be explained by a reduction of the central ion—ligand distance with pressure Preliminary results on K_2PtCl_4 are also reported

1. Introduction

Square-planar Pt(II) complexes tend to form linear stacks in the crystalline state. The distance between neighbouring central ions within one stack depends on the type of ligands and counterions and on the content of crystal water [1—4] In the tetracyano complex crystals containing crystal water. there are relatively short distances (Pt—Pt distances R between 2.8 and 3 7 Å), whereas in the tetrahalo and tetrathiocyanato complex crystals the distances have generally larger values ($R > 4$ Å) The different in-chain Pt—Pt distances of these two groups of crystals are accompanied by very different optical properties So the single-crystal tetracyano complex spectra are typical of the strong interaction between neighbouring complex ions, in contrast to the spectra ($P = 1$ bar) of the tetrahalo and tetrathiocyanato compounds which can be interpreted by a model of isolated and oriented complex ions (oriented-gas model) [5—9].

The variation of optical spectra due to high hydrostatic pressure is a well-known experimental effect and yields information about the binding relations in the solid state [10]. Spectroscopic investigations with tetracyanoplatinates exposed to high hydrostatic pressure show a drastic red-shift of the emission bands up to 320 cm^{-1}/kbar [11—14] This red-shift has been explained by a pressure-induced reduction of the Pt—

Pt distance and, therefore, by an increase of the interaction between the complex ions within a stack This effect corresponds to the spectral shift due to the variation of the Pt—Pt distance by different cations [7.14]

Here, we present linearly polarized emission spectra of $K_2Pt(SCN)_4$ single crystals exposed to high hydrostatic pressure up to 57 kbar at $T = 100$ K We look for an answer to the question whether high pressure induces a coupling between neighbouring $Pt(SCN)_4^{2-}$ ions, making their optical behavior similar to that of the tetracyanoplatinates

2. Experimental

The measurements were performed by a special spectrometer developed for investigations of the pressure dependence of linearly polarized emission and reflexion [11] The arrangement for emission measurements is similar to that described in ref. [13]. A pressure cell according to ref [12] was used To get sufficient emission intensity from $K_2Pt(SCN)_4$, the cell was cooled to $T = 100 \pm 3$ K by means of a liquid-nitrogen cooling system [11] The sample temperature is controlled by a copper—constantan thermocouple attached to the gasket. The limit of error in wavenumbers resulting from inaccuracies of temperature determination is by a factor of 50 smaller than that for the pressure determination. Small ruby crystals were used to determine the pressure within the cell The pressure

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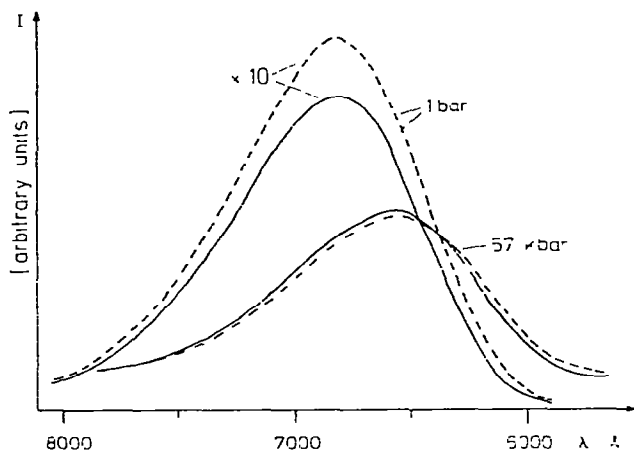Freie Universität Berlin, D-1000 Berlin, Germany

Fig 1 Polarized emission spectra of $K_2Pt(SCN)_4$ at 1 bar and 57 kbar T = 100 K Excitation wavelength λ = 514 5 nm --- $E \parallel c$ ——— $E \perp c$ (c is the stack axis, E is the electric field vector) The intensities of the 1 bar spectra given in the figure are to be multiplied by a factor of 10

shift of the R lines at T = 100 K was taken as −0 73(2) cm^{-1}/kbar [15]

Fig 1 shows the $K_2Pt(SCN)_4$ emission bands at 1 bar and 57 kbar A blue-shift of the emission maxima can be observed with pressure increase The intensity decreases considerably with increasing pressure The emission shows scarcely any dichroism in contrast to the absorption of $K_2Pt(SCN)_4$ [8 9]

Fig 2 presents the pressure dependence of the emission maxima The blue-shift is approximately linear and amounts to 10 ± 3 cm^{-1}/kbar
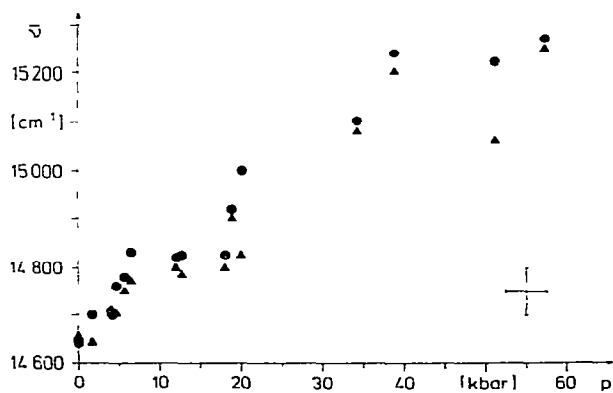

Fig 2 Energy of the $K_2Pt(SCN)_4$ emission maxima versus pressure ($\bullet$ $E \parallel c$, $\blacktriangle$ $E \perp c$)

Preliminary investigations on K_2PtCl_4 single crystals at T = 100 K yielded similar results The emission maxima ($\bar{\nu}_{max} \approx$ 12 800 cm^{-1} at p = 1 bar) are shifted to higher wavenumbers with increasing pressure by $\approx$20 cm^{-1}/kbar. The emission shift can be observed directly with the naked eye, because the emission at 1 bar is located in the infrared region and with increasing pressure a red emission appears.

3 Discussion

The short Pt—Pt distances in tetracyano complex crystals give rise to the formation of a $5d_{z^2}$-valence band and a $6p_z$ conduction band [7,8] With increasing pressure, the band gap decreases and, therefore, the emission (and the absorption) shifts to the red The pressure-induced shortening of the Pt—CN distance within a complex ion seems to be of minor importance to the optical behavior of tetracyano systems

By way of contrast, the relatively large in-chain Pt—Pt distances in $K_2Pt(SCN)_4$ (and in K_2PtCl_4) do not result in a Pt—Pt coupling identifiable in the optical energy range, just within the meaning of the model of oriented gas Therefore the pressure-induced blue-shift of the emission takes its rise from inner complex deformations

In the oriented-gas model the 14 650 cm^{-1} emission corresponds to the $^1A_{1g} \rightarrow {}^3B_{1g}$ absorption with a Stokes shift of $\approx$4250 cm^{-1} In the ligand-field approach the absorption energy is approximately [8]

$$\Delta E(^1A_{1g} \rightarrow {}^3B_{1g}) = \tfrac{20}{7} Dq + 4Ds - 12F_2 - 45F_4,$$

with the parameters (at 1 bar) F_2 = 400 and F_4 = 15 cm^{-1}, which relates to the Racah parameters B and C as $B = F_2 - 5F_4$ and $C = 35F_4$ Assuming a point-charge model [9,16] the ligand-field parameters are

$$Dq(r) \approx 2370 \text{ cm}^{-1} \times (r_0/r)^5,$$

$$Ds(r) \approx 4400 \text{ cm}^{-1} \times (r_0/r)^3.$$

with r_0 and r the equilibrium distance between central ion and ligand at 1 bar and at pressure P, respectively. Following an investigation of Zahner and Drickamer [17] on d^8(Ni) systems, we put in a rough estimate $dB/dP \approx -15$ cm^{-1}/50 kbar and set $dB/B \approx dC/C$. Then the blue-shift of 600 cm^{-1} corresponds to a

decrease of the central ion—ligand distance of $r_0 - r$ = $\Delta r \approx 0\,005$ Å (Ignoring the pressure dependence of the Racah parameters, a value $\Delta r \approx 0\,01$ Å results)
The order of this value is in agreement with Δr values measured at 50 kbar by X-ray diffraction by Al_2O_3 and MgO crystals doped with transition-metal ions, which show a similar pressure-induced blue-shift to $K_2Pt(SCN)_4$ crystals [18—20]

The observed blue-shift of the $K_2Pt(SCN)_4$ emission can be explained with the approach ligand-field theory assuming isolated oriented complex ions. This means that the optical behavior of $K_2Pt(SCN)_4$ (as well as the tetrahalo complex) crystals is determined mainly by the properties of the single complex and the interaction between the complexes can be regarded as being small due to the relatively large Pt—Pt distances in these crystals, even at high pressure

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