Spectroscopic Behaviour of Quasi-One-Dimensional Linear Chains in $MgPt(CN)_4 \cdot 7\ H_2O$ Single Crystals

HARTMUT YERSIN and GÜNTER GLIEMANN
Institut für Chemie der Universität Regensburg

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In the direction of the crystallographic *c*-axis $MgPt(CN)_4 \cdot 7\ H_2O$ has a relatively low Pt–Pt-distance (3.15 Å at 300 °K). Thus the optical behaviour shows inter-molecular interactions. Single crystal polarized emission and absorption spectra were measured between 300 °K and 5 °K. In this temperature range the emission peaks shift to the red by about 1,100 cm^{-1}. This is attributed to a decrease in Pt–Pt-distance. $MgPt(CN)_4 \cdot 7\ H_2O$ undergoes phase transitions at about 166 °K and 60 °K. To interprete the solid state emission and absorption behaviour the Davydov theory is applied. The two lowest excited bands of electronic origin are assigned to the symmetries $\Gamma_{2u}(k)$ and $\Gamma_{5u}(k)$ in the double group D_{8h}'.

1. Introduction

During the past ten years there has been considerable interest in the behavior of square planar compounds stacked above one another and forming "linear chains" in one direction[1–6]. Special interest has been applied to platinium mixed valency compounds, as they seem to be solid state conductors or semiconductors. In these crystals the Pt–Pt-distance in one direction is comparatively small (about 2.88 Å), consequently a strong interaction along the chain axis can be observed[7,8].

Of great importance, too, is the work done on crystals, where the $Pt(CN)_4^{--}$ units are built in with larger Pt–Pt-distances (3.09–3.7 Å), depending on the cations and the water content[2,3]. The interchain separation is always much larger than the Pt–Pt-distance along the chain axis. Therefore these systems show a strong physical anisotropy, which can be studied by optical spectroscopy on single crystals. Unfortunately the oscillator strengths of most of the transitions are so high, that single crystal *absorption* measurements are very difficult to do. Thus only incomplete data can be collected.

On the other hand most of the crystals exhibit a strong *emission* which depends on the Pt–Pt-distance within the chain direction[2,9–15]. But until now no reliable information was available concerning the emitting states. Therefore it seems to be interesting to study the *polarized* emission with single crystals.

We think the red $MgPt(CN)_4 \cdot 7\ H_2O$ is worth while for further study since in these crystals the Pt–Pt-distance at room temperature is only 3.15 Å and so some solid state effects should be seen. The information found in the literature is contradictory.

2. Experimental Section

The apparatus for studying single crystal polarized emission is described elsewhere in detail[17]. The crystals can be cooled down from room temperature to liquid helium temperature. They are stuck by the use of silver paste on a copper plate, which can be inserted in the cryostat. This cryostat has very restricted dimensions. It is mounted on a revolving stage of a polaristion microscope and can be turned around, when a flexible liquid helium line is used.

For excitation an argon laser (Spectra-Physics Mod. 165) with filters supressing the plasma light was applied. The emission was observed at the excitation side*. For polarisation a Glan prism was used. Just behind the spectrograph (Spex 1401) we mounted the photomultiplier (RCA C 31 034). For signal processing the photon counting technique (SSR–PAR) was applied. The photomultiplier was cooled down to —30 °C by a Durchflußkühler[17].

The polarized single crystal absorption was measured with the same apparatus. The crystals

Requests for reprints should be sent to Dr. HARTMUT YERSIN or Prof. Dr. GÜNTER GLIEMANN, Institut für Chemie der Universität, *D-8400 Regensburg*, Universitätsstraße 31.

* The angle between incident beam and observation direction was about 40°.

mounted in the cryostat were illuminated with an iodide quartz lamp.

$MgPt(CN)_4$ was prepared according to the literature[18,19]. We received $MgPt(CN)_4 \cdot 7\ H_2O$ crystals from aqueous solution by slowly evaporating the water. They had the typical red respectively green-metallic lustre. We easily got good single crystals up to dimensions of $0.2 \times 0.2 \times 0.4$ mm³.

Chemical analysis:

Found	C 11.0	H 2.9	N 12.5,
Calcd	C 10.7	H 3.1	N 12.5.

3. Crystal structure

A complete crystal structure is not available for $MgPt(CN)_4 \cdot 7\ H_2O$ even at room temperature. But it is known[3, 20–22], that the crystals have tetragonal symmetry. The $Pt(CN)_4^{--}$ molecules have D_{4h} symmetry. They are stacked one above the other and form linear chains with Pt–Pt-distances of 3.15 Å (at 300 °K). The unit cell dimensions (at 300 °K) are $a = b = 14.537$ Å, $c = 6.310$ Å, $Z = 4$. c is the chain axis. The rotation angle between neighbouring molecular planes is 45°. The watermolecules and Mg^{2+} lie between different chains.

4. Results

Fig. 1 shows the polarized *emission* spectra* for $MgPt(CN)_4 \cdot 7\ H_2O$ single crystals at four different temperatures. Lowering the temperature an obvious red shift of the peak positions and a change in polarized intensities can be seen. We did not observe any variation of the spectra when we changed the excitation wave length.

Fig. 1 as well shows the polarized *absorption* in the low energy region at 295 °K and 78 °K. Since our crystals were too thick, we only measured the $\vec{E} \perp c$ spectra and the low energetic absorption tails for the $\vec{E} \parallel c$ direction.

In Fig. 2 we plotted the half widths and the peak positions of the $\vec{E} \parallel c$- and $\vec{E} \perp c$-emission spectra *versus* reciprocal temperature. This Figure also

* Our spectra are not corrected to the response of the apparatus. But the photomultiplier RCA C 31 034 has a flat quantum efficiency curve in the region of interest. Thus in this respect the apparatus does not effect an essential spectral error. On the other hand the emission is reabsorbed to a certain amount, if the absorption band overlaps the emission, even with the reflection method[23]. This should be kept in mind when regarding the spectra. The polarisation error is about 5%.

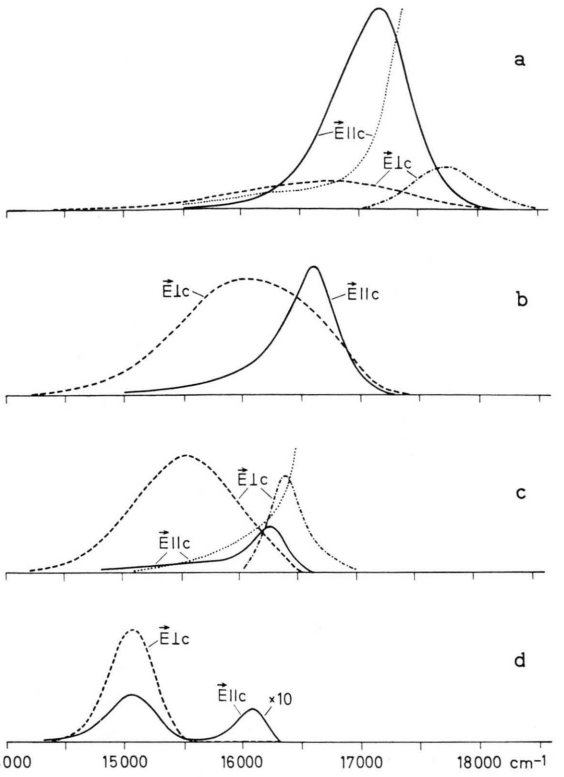

Fig. 1. Polarized emission and absorption of $MgPt(CN)_4 \cdot 7\ H_2O$ single crystals at different temperatures.

a. emission: 300 °K, absorption: 295 °K;
b. 197 °K;
c. emission: 125 °K, absorption: 78 °K;
d. 5 °K.

Emission data:

Excitation wavelength: 457.9 nm;
Spectral bandwidth: 10 cm^{-1}.

The intensities at different temperatures are not comparable. The scale is linear in intensity. The $\vec{E} \parallel c$-emission intensity at 5 °K (d) is multiplied by a factor of 10.

$\vec{E} \parallel c$-spectra: ———

$\vec{E} \perp c$-spectra: – – – –

Absorption data:

The absorption scale is linear in extinction. The $\vec{E} \perp c$ absorption curves are intensified by a factor of $\frac{2}{5}$ compared with the $\vec{E} \parallel c$ curves.

Crystal thickness: 7 μm;

Spectral bandwidth: 0.5 cm^{-1}.

$\vec{E} \parallel c$-spectra: . . . . . .

$\vec{E} \perp c$-spectra: - - - - - -

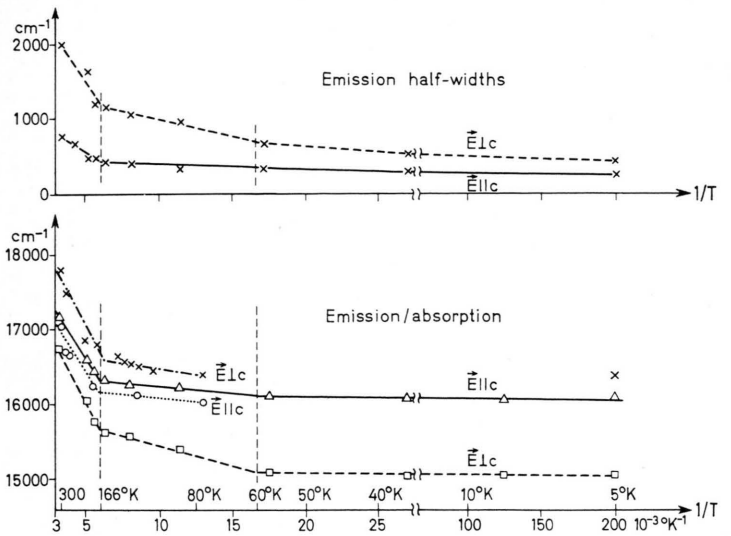

Fig. 2. Polarized emission and absorption data for $MgPt(CN)_4 \cdot 7\ H_2O$ single crystals *versus* reciprocal temperature.

Emission data:
Peak positions } $\vec{E} \parallel c$: ———
Half widths } $\vec{E} \perp c$: – – – –

Absorption data:
Peak positions* $\vec{E} \perp c$: – . – . –
Low energetic edge positions $\vec{E} \parallel c$: .....

* The point at 5 °K in the $\vec{E} \perp c$ absorption spectrum is taken from ref. [37].

shows the spectral shift of the absorption peak positions of $\vec{E} \perp c$ and the positions of the low energy absorption edge for $\vec{E} \parallel c$.

5. Discussion

5.1 Single ion

The assignment of the electronic structure of the single $Pt(CN)_4^{--}$ ion is contradictory in literature[2, 24–28]. But there is little disagreement about two important points: 1. The lowest excited one-electron molecular orbital has a_{2u} symmetry and 2. the highest filled one-electron orbitals are more or less metal d-orbitals with gerade symmetry. Therefore the lowest transition is an electric dipole one, which is strongly allowed without the need of asymmetric vibration coupling.

The $Pt(CN)_4^{--}$ molecular symmetry is supposed to be D_{4h}. The electric dipole vector transforms in D_{4h} as A_{2u} (normal to the molecular plane) and as E_u (lying within the plane). As the many-electron ground state has $^1A_{1g}$ symmetry* it follows that the transitions $^1A_{1g} \rightarrow {}^1A_{2u}$ and $^1A_{1g} \rightarrow {}^1E_u$ are fully allowed. These correspond to the one-electron transitions

$a_{1g}(d_{z^2}) \rightarrow a_{2u}(p_z, CN\pi^*)$ and $e_g(d_{xz}, d_{yz}) \rightarrow a_{2u}(p_z, CN\pi^*)$, respectively**.

* See for example[24–28].

** The notation in brackets means that in $Pt(CN)_4^{--}$ an extensive orbital delocalisation is present, consequently the transitions regarded, are charge transfer transitions.

In single crystals, where the molecules lie oriented, a group theoretical assignment would be very easy with non-interacting molecules by the use of polarized absorption measurements. But the interaction between different molecules within the chain direction cannot be neglected. Therefore the group theoretical symmetry analysis is not to be done straight forwardly.

5.2 Solid state

5.2.1 Factor group splitting

The strong influence of the inter-molecular interaction in $MgPt(CN)_4 \cdot 7\ H_2O$ is indicated by comparing the absorption spectra of the solution and the single crystals. In solution the absorption peak at 46,100 cm^{-1} probably can be assigned to $^1A_{1g} \rightarrow {}^1A_{2u}$[24,25,28]. In $MgPt(CN)_4 \cdot 7\ H_2O$ the corresponding absorption peak lies approximately at 18,800 cm^{-1} ***. This means that the solid state effect causes an energy shift of about 27,300 cm^{-1}, which is in the same order of magnitude as the ligand field splitting itself[29].

One possible approach to understand the single crystal properties is the use of the Davydov or factor group splitting model[30–33]. This has already been proposed[4,5,16].

*** This is the mean value between the low and the high energetic absorption edge (not reported in Fig. 1). See also section 5.2.2.

In $MgPt(CN)_4 \cdot 7\ H_2O$ the molecular interaction along the chain axis is very much higher than between different chains (section 3.). This we take as a justification for reducing the crystallographic unit cell so, that just two $Pt(CN)_4^{--}$ ions – lying along the chain axis – are to be considered.

We get a new linear unit cell with the cell dimension c. The two planar molecules are $c/2$ apart from each other and are turned around the c-axis by an angle of 45°. The molecular symmetry D_{4h} is not altered. The crystallographic site symmetry is D_{4h}, too.

The factor group is found by adding special symmetry elements to that space group, which corresponds to the site group. These special elements required transform one molecule of the unit cell in the other one. Here we need a fractional translation of $c/2$ combined with 45° rotations around c. This is a C_8 screw axis. The point group which is isomorphous to this one-dimensional factor group than is D_{8h}*.

The energy states of the one-dimensional crystal must be classified according to the symmetry group D_{8h}. Every excited molecular state will give two crystal states, because two translational non-equivalent molecules belong to the unit cell.

We have now to determine the irreducible factor group representations of these two crystal states. The character of the symmetry operation R in the reducible factor group representation is given by H. WINSTON[34]

$\chi^{f.g.}(R) = \Sigma_a \delta_a(R) \chi^{s.g.}(R)$
$\delta_a = 1$ if R is an element of the site group in site a
$\delta_a = 0$ otherwise.

$\chi^{s.g.}(R)$ is the character of the site group. The summation index runs over all translational non-equivalent sites in the unit cell.

It is quite easy to find the irreducible representations by using the D_{8h} character table[34]. For example the molecular term $^1A_{2u}$ splits into $^1A_{2u}$ and $^1B_{2u}$. The term ^1E_u splits into $^1E_{1u}$ and $^1E_{3u}$. Only transitions from the ground state $^1A_{1g}$ to $^1E_{1u}$ and $^1A_{2u}$ are fully allowed in D_{8h} because the electric dipole vector transforms as $A_{2u}(z)$ and $E_{1u}(x,y)$.

* For simplicity the point group which corresponds to the factor group often is also termed factor group.

Because of the translational symmetry the factor group splitting components give dispersion curves $^1A_{2u}(\vec{k})$ and $^1E_{1u}(\vec{k})$, where $\vec{k}$ is the wave vektor**.

5.2.2 Assignments

The very strong *absorption* in the $\vec{E} \parallel c$ direction, of which only the low energetic absorption tail is shown in Fig. 1, corresponds to a direct of fully allowed transition between the ground state valence band $\Gamma_{1g}(^1A_{1g})$ and the $\Gamma_{2u}(^1A_{2u})(k)$ band***. k equals the photon momentum. This assignment is supported by the selection rules developed in the last section. Further arguments are the high absorption intensity and the missing of temperature dependence, the strong overlap of emission and absorption, and the low lifetime of the corresponding emission[36].

It does not seem to be easy to evaluate the factor group splitting energy, which is in our model responsible to the often discussed "red shift" of the crystallized $Pt(CN)_4^{--}$ compounds compared with the single ion. The reason is that our knowledge about the interaction potential is limited. MONCUIT[16] showed that the dipole-dipole interaction only gives an energy "shift" of about 10,000 cm^{-1} compared with 27,300 cm^{-1} "red shift" here.

The absorption band of much lower intensity in the $\vec{E} \perp c$ spectrum (Fig. 1) is assigned to a symmetry allowed singlet→triplet**** transition, which gains it's intensity by spin-orbit coupling*****. The triplet character is suggested by the lower intensity of this transition and the relatively long lifetime of the corresponding emission (100 μsec[36]). The selection rules require an assignment of this state to Γ_{5u} in D'_{8h}-double group. The symmetry must be ungerade****** because the transition

** Since the space group only has one dimension we write k instead of $\vec{k}$.

*** Here we use the D'_{8h} double group notation analog to Bethe's notation. The symmetry symbols written in brackets give the main component of the corresponding eigenvector.

**** The spin is not a good quantum number. We use this expression only for simplicity.

***** The free Pt^{2+} ion spin-orbit parameter is about 4000 cm^{-1} and is suspected to be reduced to about 3000 cm^{-1} in $Pt(CN)_4^{--}$ [28].

****** See also section 5.1.

probability does not change very much even when lowering the temperature down to 5 °K[37]. Here we do not try to estimate quantitatively the mixing coeffients of the eigenvector Γ_{5u}. But it can be stated, that Γ_{5u} is composed by different components, as for example $\Gamma_{5u}(^3A_{2u})$ and $\Gamma_{5u}(^1E_{1u})$. The singlet component responsible for the intensity mechanism will be comparatively low, because $^1E_{1u}$ lies at much higher energies. Consequently the intensity of the corresponding transition is relatively low*. It must be noted that here, too, we do not have a single Γ_{5u} level but a $\Gamma_{5u}(k)$ dispersion curve.

We do not find the $^1E_{1u}(k)$ band within the spectral region studied. The reason is, the spectral position does not change very much, when the Pt–Pt-distance is reduced[2]. Consequently the corresponding inter-molecular interaction potential will be relatively small.

The assignment of the solid state *emission* generally is a little more complicated than the assignment of the absorption, because the excitation relaxes very fast (in 10^{-12} sec) to the lowest excited state (or to the ground state). – The lowest excited state need not to lie in the region $k = 0$ of the Brillouin zone. Therefore the emission depends on the zone structure**. For $MgPt(CN)_4 \cdot 7\ H_2O$ single crystals the absorption and emission spectra overlap in $\vec{E} \| c$ and in $\vec{E} \perp c$. Further they shift simultaneously – still overlapping – to lower energies when lowering the temperature***. It follows that the emission here comes from near the center of the Brillouin zone****.

These two results show that the observed emission bands just correspond to the observed absorption bands $\Gamma_{2u}(^1A_{2u})(k)$ and $\Gamma_{5u}(k)$. The polarized emission follows the same selection rules as the absorption*****. Fig. 3 gives the relative positions of the energy levels discussed here.

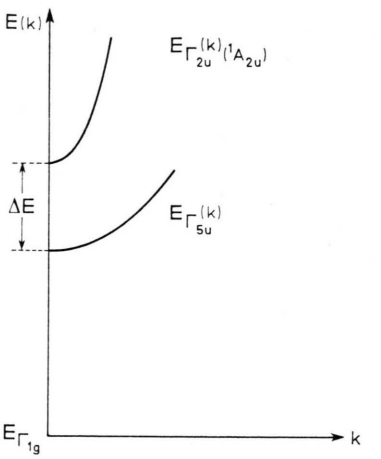

Fig. 3. Energy bands for $MgPt(CN)_4 \cdot 7\ H_2O$ in terms of the group D_{8h}. The diagram only shows the relative band position in the Brillouin zone near $k = 0$.
The electric dipole selection rules in D_{8h} are:

$$\Gamma_{1g} \leftrightarrow \Gamma_{2u}: \vec{E} \| c;$$
$$\Gamma_{1g} \leftrightarrow \Gamma_{5u}: \vec{E} \perp c.$$

5.2.3 Temperature behaviour

5.2.3.1 Red shift: The temperature behaviour of the emission and absorption data is an enormous source of further information. One general feature of the spectra is a red shift when lowering the temperature from 300 °K to 5 °K (Fig. 2). This is attributed mainly to reduced Pt–Pt-distances, which involve an increasing interaction potential and consequently a larger factor group "red-shift"[38].

5.2.3.2 Phase transition: The plot of some independent physical properties versus reciprocal temperature shows two temperature points where the slope changes obviously. The first one lies near 166 °K and the second one near 60 °K******. This is confirmed by all the parameters studied: Emission half-widths, absorption peak and edge positions

* The free ion mixing coeffients are discussed in ref. [24,28].

** See for example ref. [32].

*** This is to be seen when regarding the energy shift of the peak positions in the $\vec{E} \perp c$ spectra from 300 °K to 77 °K. In both – emission and absorption – the red shift is 1400 cm^{-1}. To compare the $\vec{E} \| c$ spectra we used the emission peak positions and absorption edge positions. In both cases we found a red shift of 950 cm^{-1} for the same temperature variation. (See Fig. 2 as well.)

**** We can neglect defect emission, since the emitting bands corresponds to the absorbing bands.

***** The 5 °K $\vec{E} \| c$ emission shows two peaks (Fig. 1d). The low energetic one has the same half width and peak position as the $\vec{E} \perp c$ peak, and its intensity is about 5% of the $\vec{E} \perp c$ intensity. Therefore we attribute it to the polarisation error.

****** We did not yet establish the exact value of th transition temperature. Therefore we must consider an experimental error of about ± 10%.

(Fig. 2), emission lifetime[36], relative emission intensities (Fig. 4) and tentatively measured birefringence*. We suggest that at the reported temperatures phase transitions take place. They are not drastic because the crystals do not break, when passing over the critical temperatures. Further the selection rules do not seem to change. We suppose therefore that the one-dimensional space group is not altered.

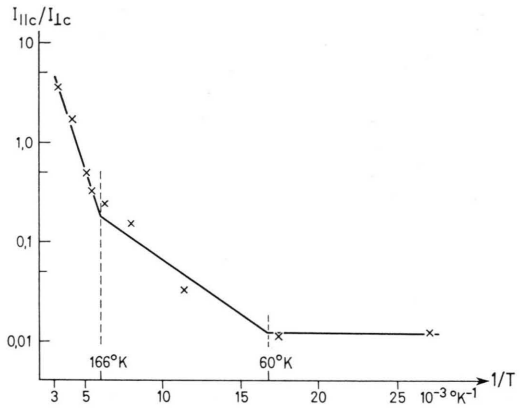

Fig. 4. Polarized emission data for $MgPt(CN)_4 \cdot 7\ H_2O$ single crystals. Relative intensities $I_{\parallel c}/I_{\perp c}$ *versus* reciprocal temperature.

5.2.3.3 Changes in polarized emission: Fig. 1 shows an extreme sensitivity of the polarized emission to temperature changes even within the range, where the crystallographic phase does not change. Fig. 4 summarizes these results. The relative emission intensities are plotted *versus* reciprocal temperature.

At low temperature there is only very little $\vec{E} \parallel c$-emission intensity compared with the $\vec{E} \perp c$ intensity. Consequently Γ_{5u} lies at $k = o$ lower in energy than Γ_{2u} (Fig. 3). Rising the temperature $\Gamma_{2u}(k)$ is populated according to a Boltzmann factor. As a result an increasing $\vec{E} \parallel c$-emission intensity ($I_{\parallel c}$) is seen. The relative intensity is

$$\frac{I_{\parallel c}}{I_{\perp c}} \sim \frac{P(\Gamma_{2u})}{P(\Gamma_{5u})} \cdot \exp(-\Delta E/k_B T).$$

P are the probabilities for emission processes, they are proportional to the squares of the corresponding absorption transition moments. ΔE is the energy difference according to Fig. 3 and k_B the Boltzmann constant.

Since $\Gamma_{2u}(k)$ is strongly allowed $I_{\parallel c}$ dominates at room temperature (Figs. 1a and 4)**.

The variation of the relative intensities with temperature is not as is supposed by the influence of the exponential Boltzmann factor alone. The reason is, ΔE changes with every phase transition. From the slopes of the plot in Fig. 4 two ΔE values are found. The low temperature slope is too inaccurate here and therefore this one is taken from ref[36]. We found the following values for the energy difference of the two emitting bands at $k = o$.

$$\left.\begin{aligned} \Delta E\ (300\ °K - 166\ °K) &= 760\ cm^{-1} \\ \Delta E\ (166\ °K - 60\ °K) &= 170\ cm^{-1} \\ \Delta E\ (60\ °K - 5\ °K) &= 18\ cm^{-1} \end{aligned}\right\} \pm 15\%$$

The diminution of ΔE with temperature seems to be a consequence of a reduction in Pt–Pt-distance along the chain axis[38].

5.2.3.4 Band shapes: The peak positions and the half-widths of the observed transitions in emission also show a characteristic temperature behaviour, which is different for the two polarisations (Fig. 2). We tried to explain these features only by taking into account the configurational coordinate model*** with different shifts of the potential hyper-surfaces. But this model failed completely. Therefore we assume different**** band structures for the two emitting bands in the region $k = o$. The $\Gamma_{5u}(k)$ band is expected to be much flatter than the $\Gamma_{2u}(k)$ band (Fig. 3). Thus the different slopes in half-widths *versus* reciprocal temperature are explained straight forwardly in the following way:

A given thermal energy $k_B \cdot T$ causes a population of the excited states within the same band. This corresponds to a certain populated range Δk. Δk is large for the $\Gamma_{5u}(k)$ band compared with the corresponding Δk in the $\Gamma_{2u}(k)$ band. Consequently in an emission process with a $\Gamma_{5u}(k)$

* Not reported here.

** In ref. [39] we discussed to a greater extent the Boltzmann population of $^4T_{2g}$ *via* ^2E_g in the example of $[Cr\ urea_6]X_3$ single crystals. See also ref. [40].

*** See for example ref. [41].

**** This is not unexpected because the two bands have different electronic origin.

origin more phonons are available which fullfill the momentum selection rules. As a result a broad emission is observed (Figs. 1a and 2). Lowering $k_B \cdot T$ a reduction of the populated Δk range influences much more the $\Gamma_{5u}(k)$ than the $\Gamma_{2u}(k)$ emission. A more evident half-width reduction follows for the $\Gamma_{5u}(k)$ emission ($\vec{E} \perp c$) (Fig. 2).

The energy difference of the two emission peaks *increases* from about 400 cm^{-1} (300 °K) to 1,000 cm^{-1} (5 °K) though it is shown that the energy difference between $\Gamma_{2u}(o)$ and $\Gamma_{5u}(o)$ *decreases* from 760 cm^{-1} (300 °K) to 18 cm^{-1} (5 °K). Further on the energy difference of the absorption and emission peak positions (stokes shift) in the $\vec{E} \perp c$ spectra does not change within the temperature range regarded. This behaviour cannot be understood without taking into account an energy dispersion of the electronic and the phonon branches. This is a further hint that it is not possible to explain the $MgPt(CN)_4 \cdot 7\ H_2O$ properties only by "red shifted molecular levels".

Finally some remarks on the asymmetry in the emission spectra*: Fig. 1b shows this clearly for the $\vec{E} \parallel c$ spectrum. Such an asymmetry can already be explained in the case of single molecules if the difference in the equilibrium positions of the ground state and the excited state is small. It follows an asymmetric Poisson like curve[42]. The reason is that during the emission process molecular ground state vibrations are excited simultaneously. This seems to be the case here. The coupled vibrations may be local excitations.

6. Conclusions

To explain the experimental data found for $MgPt(CN)_4 \cdot 7\ H_2O$ we have developed a simple model which includes some solid state interactions along the crystallographic c-axis. Though this Davydov or factor group splitting model succeeded fairly well qualitatively we think good quantitative results should refine the Davydov approximation. Further on an inter-chain coupling should be introduced which certainly is of great importance to the observed phase transitions.

* The polarisation error of 5% is not large enough to be responsible for the observed asymmetry.

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