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PRESSURE EFFECT ON OPTICAL SPECTRA AND ELECTRICAL RESISTIVITY OF SOME Pt-COMPLEXES

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$K_2Pt(CN)_4 \cdot 3H_2O$, $MgPt(CN)_4 \cdot 7H_2O$ and $BaPt(CN)_4 \cdot 4H_2O$ exhibit an anomalously large red shift both of the absorption and luminescence spectra with hydrostatic pressure and a continuous decrease of the electrical resistivity by a factor of approximately 10^{-4} up to 180 kbar.

The electrical and optical properties of quasi-one-dimensional solids such as TCNQ ion salts1) and square planar complexes of platinum2) at high pressures have been a subject of interest.

Pressure effect on the absorption and luminescence spectra, and the electrical resistivity of some Pt-complexes, $K_2Pt(CN)_4 \cdot 3H_2O$, $MgPt(CN)_4 \cdot 7H_2O$ and $BaPt(CN)_4 \cdot 4H_2O$, which are composed of quasi-one-dimensional Pt-chains, has been studied at room temperature. These complexes exhibit an anomalously large shift to lower frequency (red shift) both of the absorption and luminescence spectra with hydrostatic pressure and a continuous decrease of the electrical resistivity by a factor of approximately 10^{-4} up to 180 kbar.

The Pt-complexes were prepared as described in the literature.3a,b) The visible absorption and emission spectra of polycrystalline samples were measured at hydrostatic pressures up to 5.4 kbar.

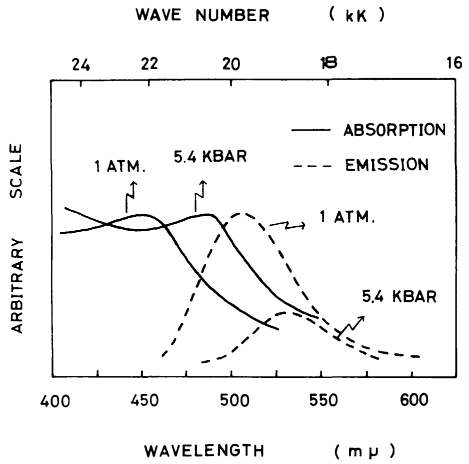

Figure 1.

Pressure effect on the absorption and luminescence spectra of polycrystalline $BaPt(CN)_4 \cdot 4H_2O$

Table 1.

Absorption and emission maxima in the visible region, red shift and Pt-Pt distance

Material	Absorption maximum mμ (kK)	Red shift (cm^{-1}/ kb)	Emission maximum mμ (kK)	Red shift (cm^{-1}/ kb)	Pt-Pt distance (A)
$K_2Pt(CN)_4 \cdot 3H_2O$	382 (26.2)	- 250	437.5 (22.9)	- 130	> 3.35[a]
$BaPt(CN)_4 \cdot 4H_2O$	450 (22.2)	- 315	505 (19.8)	- 167	3.32[b]
$MgPt(CN)_4 \cdot 7H_2O$	555 (18.0)	- 389			3.16[b]

a. S. Yamada, Kagaku ; 41 , No. 12 , 651 (1971)

b. ref. 3 (c)

Figure 1 shows the effects of pressure on the absorption and on the luminescence spectra of the Ba-salt. These electronic spectra at atmospheric pressure agree with the work of Moncuit and Poulet[4). The absorption peak of 450 mμ showed an anomalously large red shift with increasing pressure, in a rate of -315 cm^{-1}/ kbar. The remarkable red shift was also found for the K and Mg salts. These results are summarized in Table 1. It should be noted that the complexes with the shorter Pt-Pt distance exhibit the larger shift.

The emission band of 505 mμ at atmospheric pressure shifted to 530 mμ at 5.4 kbar. The rate of the red shift with pressure is -167 cm^{-1}/ kbar, which is about half in comparison with that for the absorption band. The emission intensity decreased with increasing pressure. The optical behavior was reproducible at room temperature. The similar result was observed for the K salt.

The electrical resistivity of polycrystalline $MgPt(CN)_4 \cdot 7H_2O$ has been measured as a function of pressure up to 180 kbar at room temperature, using a supported-taper piston apparatus.5) The resistivity versus pressure curve is shown in Figure 2. The resistivity decreased continuously by a factor of approximately 10^{-4} with increasing pressure up to 180 kbar. With decreasing pressure it increased rapidly to the room temperature value at zero pressure in the low pressure region. The remarkable pressure dependance of the resistivity seems to be closely related to the anomalous large red shift in the complex.

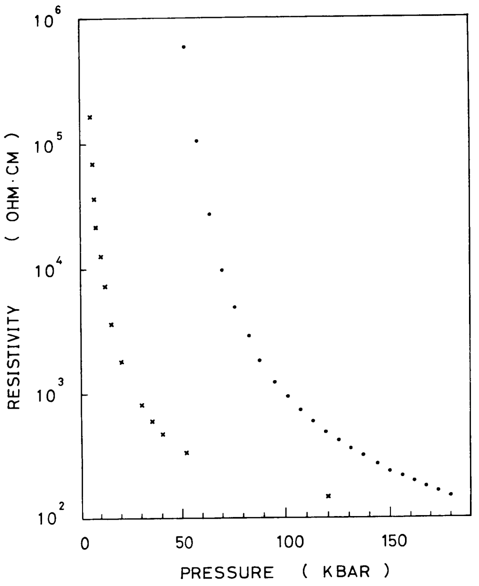

Figure 2.

Pressure effect on the electrical resistivity of polycrystalline $MgPt(CN)_4 \cdot 7H_2O$

The symbol • refers to data upon pressure loading, while × refers to one upon pressure unloading.

Bundy et al have investigated the X ray diffraction and the conductivity for $K_2Pt(CN)_4Br_{0.3}\cdot 2.3H_2O$, $Pt(NH_3)_4PtCl_4$ (Magnus' green salt) and $Ir(CO)_2(acac)$ at high pressures[2]. The lattice constant and the metal-metal distance in d^8 metal complexes decrease with increasing pressure.
The maximum in the conductivity versus pressure curve has been observed. However, in the case of Mg-salt the conductivity maximum was not found up to 180 kbar.

Acknowledgment

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