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EPR Evidence for Metal-Insulator Transition in the "One-Dimensional" Platinum Complex $K_2Pt(CN)_4Br_{1/3} \cdot 3H_2O$

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Electron paramagnetic resonance has been observed in the mixed-valency platinum complex $K_2Pt(CN)_4Br_{1/3} \cdot 3H_2O$. The g factors observed are characteristic of d_{z^2} -like hole states. The variation of the observed signal intensity is not consistent with the interrupted-strand model or the disorder model but is in accord with the predictions of the Peierls-distortion model.

The mixed-valency platinum complexes (MVPC), such as $K_2Pt(CN)_4Br_{1/3} \cdot 3H_2O$ and their organic counterparts [charge-transfer complexes of tetracyanoquinodimethane (TCNQ)], have attracted considerable attention lately¹⁻¹¹ as a result of their high "one-dimensional" electrical conductivities and the possibility that their base structures [$Pt(CN)_4$ or TCNQ chains] can be used as "spines"¹² for the synthesis of high-temperature superconductors. However, there are several areas of disagreement on the properties of these compounds: There is a controversy with regard to the nature of conduction. Simple band-theory arguments,¹ optical and infrared reflectivity measurements,⁴ and the observation of the giant Kohn anomaly⁵ seem to indicate delocalized states and metallic conduction. On the other hand, non-metallic dc-conductivity⁸ measurements and theories¹³ on disordered one-dimensional systems favor localized states and hopping conduction. In order to reconcile these contradictions at least three models have been proposed: the "defect" or interrupted-strand model,^{4,5} the "disorder" model,⁹ and the "distortion" or Peierls-Kohn

instability model. Recent x-ray diffuse-scattering experiments by Comes *et al.*,⁶ coherent inelastic-neutron-scattering experiments by Renker *et al.*,⁶ as well as the theoretical work of Rice and Strässler,⁶ favor the "distortion" model. Another question is the nature of the highest occupied band in this compound. It has been surmised¹ (but not yet experimentally verified) that this band is of d_{z^2} character. In a previous paper¹⁴ we have shown that in the "one-dimensional" semiconductor Magnus's green salt (MGS), $Pt(NH_3)_4PtCl_4$, the highest-lying band is indeed d_{z^2} like. There is also a disagreement about the sign of the carriers in MVPC.⁷

In the present paper we report on the observation of EPR in the MVPC $K_2Pt(CN)_4Br_{1/3} \cdot 3H_2O$. The results show that the observed magnetic centers are holes in d_{z^2} -like states. The temperature variation of the line intensity can be explained in terms of the "distortion model" and is in contradiction with the "defect" and the "disorder" models.

The single crystals of $K_2Pt(CN)_4Br_{1/3} \cdot 3H_2O$ used in this study were of typical size 3 mm

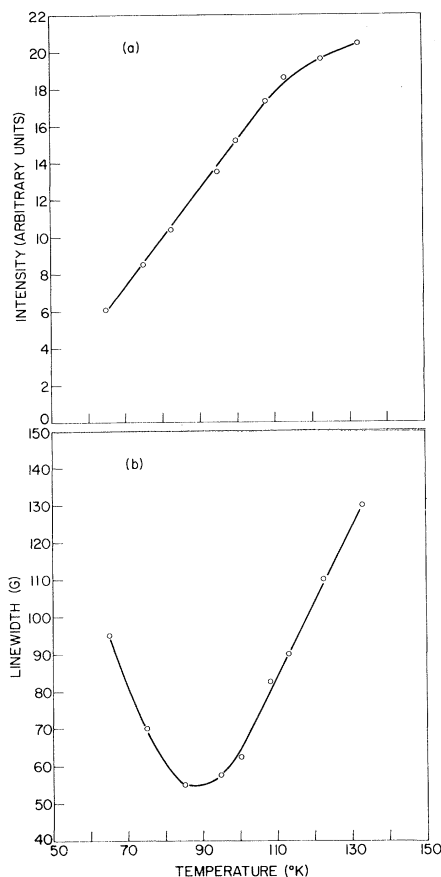


FIG. 1. (a) Temperature variation of EPR signal intensity. (b) Temperature variation of the linewidth.

$\times \frac{1}{2} \text{mm} \times \frac{1}{4} \text{mm}$. From the EPR signal intensities we estimate $\sim 10^{20}$ spins/cm³ at $T \sim 85^\circ\text{K}$ in *freshly prepared crystals*. The intensities decrease if the crystals are allowed to age in the laboratory environment. It is known² that crystals of $\text{K}_2\text{Pt}(\text{CN})_4\text{Br}_{1/3} \cdot 3\text{H}_2\text{O}$ lose water at relative humidities $\leq 55\%$ at room temperature.¹⁵ The intensities also decrease with decreasing temperatures [Fig. 1(a)]. The measurements were performed at X-band frequencies. The observed spectra can be fitted by the axial-spin Hamiltonian

$$\mathcal{H} = \mu_B [g_{\parallel} S_z H_z + g_{\perp} (S_x H_x + S_y H_y)]$$

with spin $S = \frac{1}{2}$. Figure 2 shows the angular variation of the g value, and Fig. 3 shows the spectrum at $T = 85^\circ\text{K}$ with the magnetic field perpendicular to the c axis. The line shape is Lorentzian. The measured g values are

$$g_{\parallel} = 1.946 \pm 0.005, \quad g_{\perp} = 2.336 \pm 0.005.$$

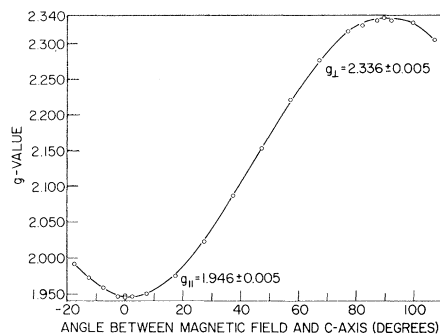


FIG. 2. Angular variation of the g factor.

As in the case of MGS^{14} the magnitudes of the g values are characteristic of d_{z^2} -like hole states with an admixture, due to spin-orbit interaction, of the degenerate $e_u(5d_{xz, yz})$ states. Other symmetries such as p_x , $d_{x^2-y^2}$, d_{xy} , etc. do not yield values in agreement with the observed magnitudes.¹⁶ From the magnitudes of the g values alone, however, one cannot determine whether the holes are in d_{z^2} bands, are self-trapped, or are captured by the Br^- ions.

Comparison of the measured values with the second-order perturbation theoretical formulas¹⁶

$$g_{\parallel} = 2N^2 - 3N^2(\zeta/\Delta E)^2,$$

$$g_{\perp} = 2N^2 + 6N(\zeta/\Delta E) - 6N^2(\zeta/\Delta E)^2$$

gives $N \approx 0.99$, $\zeta/\Delta E \approx 0.067$, where N is the normalization factor for the zeroth-order wave function following spin-orbit interaction, ζ is the spin-orbit parameter of Pt ions in the crystal, and ΔE is the energy separation between $a_{2u}(5d_{z^2})$ and the degenerate $e_u(5d_{xz, yz})$ states. Unlike

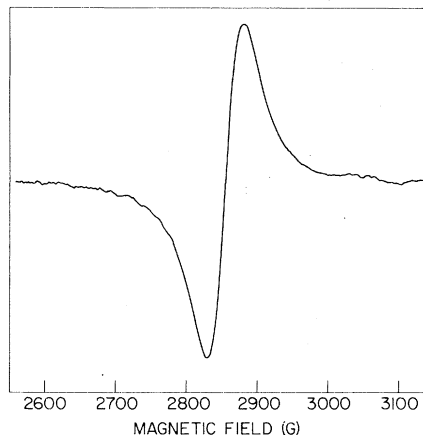


FIG. 3. EPR spectrum at $T = 85^\circ\text{K}$ and $H \perp c$ axis.

"extrinsic" MGS,¹⁴ no hyperfine pattern was observed for $K_2Pt(CN)_4Br_{1/3} \cdot 3H_2O$.

In order to gain insight into the nature of the conduction and to distinguish between the band or bound character of the carriers, we have studied the temperature variation of the line intensity and linewidth. Figure 1(a) shows the variation of the signal intensity defined as (the peak-to-peak amplitude of the first-derivative signal) \times (linewidth)² as a function of temperature. The intensity increases with temperature. This type of variation is in contradiction with the "defect"^{4,5} and the "disorder"⁹ models. In both of these models one would expect a nonzero paramagnetic signal intensity which is a decreasing function of temperature at the lowest temperatures. The experimental results can, however, be reasonably explained in terms of the "distortion" model.⁶ In this model, as a result of a second-order metal-insulator transition, one expects a low-temperature diamagnetic behavior. A linear extrapolation of the intensity-versus-temperature curve [Fig. 1(a)] indicates that at $T \sim 40^\circ K$ this material appears to become completely diamagnetic. Available conductivity data² show a maximum in conductivity at $\sim 250^\circ K$, and that below $\sim 40^\circ K$ the crystal is a perfect insulator. At the intermediate temperatures, $40 \lesssim T \lesssim 250^\circ K$, the apparent conductivity energy gap is a decreasing function of temperature.² The EPR signals observed also indicate that a gradual transition occurs over a broad *transition region*. Therefore no one temperature can be defined as the *transition point*.

Figure 1(b) shows the variation of the linewidth with temperature. The decrease of the linewidth with increasing temperature at temperatures $T \lesssim 80^\circ K$ and the Lorentzian line shape may be attributed to motional narrowing due to hopping of the holes among bound states.¹⁷ At high temperatures, $T \gtrsim 90^\circ K$, the linewidth increased with temperature. A possible mechanism which could lead to such behavior is the hole-phonon collision broadening.¹⁸ The two competing processes cause the linewidth to go through a minimum of ~ 55 G at $\sim 85^\circ K$. The absence of hyperfine structure can thus be attributed to the fact the holes are not tightly bound in the temperature region where they are observed.

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