

## EPR INVESTIGATION OF THE SPIN RELAXATION IN THE QUASI-ONE-DIMENSIONAL PLATINUM CONDUCTORS\*

L. V. Giurgiu, X. Filip, O. Pana, C. Filip, A. Darabont<sup>a</sup>, R. Ordean, S. Knorr<sup>b</sup>, J. Rahmer<sup>b</sup>, M. Mehring<sup>b</sup>

National Institute for Research and Development of Isotopic and Molecular Technology, P.O. Box 700, R-3400 Cluj-Napoca, Romania

<sup>a</sup>Faculty of Physics, Babes-Bolyai University, R-3400 Cluj-Napoca, Romania

<sup>b</sup>2. Physikalisches Institut, Universität Stuttgart, 70550 Stuttgart, Germany

Multi-frequency EPR investigations of  $\text{Rb}_2\text{Pt}(\text{CN})_4\text{Br}_{0.3}(\text{FHF})_{0.4}$  quasi-one-dimensional conductor are presented. The angular dependencies of the effective spin-spin relaxation rate,  $(T_2)^{-1}$ , are discussed in terms of the solitonic model. The relaxation of the spin carrying solitons is dominated by the hyperfine mechanism.

(Received July 15, 2000; accepted November 15, 2000)

*Keywords:* Quasi-one-dimensional molecular conductors, High-frequency EPR, Spin-relaxation, Soliton model

### 1. Introduction

The outstanding features associated with the quasi-one-dimensional (Q1D) platinum conductors are the anisotropic physical properties, a Peierls transition accompanied by a giant Kohn anomaly and a Frölich charge density wave (CDW). Besides  $\text{K}_2\text{Pt}(\text{CN})_4\text{Br}_{0.3} \cdot 3.2\text{H}_2\text{O}$ , KCP(Br), the platinum chain compounds family, which is very large, remains far less explored. We will focus on the anhydrous  $\text{Rb}_2\text{Pt}(\text{CN})_4\text{Br}_{0.3}(\text{FHF})_{0.4}$ , RbCP(FHF), for the following reasons: (i) despite a smaller interchain distance ( $d_{\perp}$ ) than in KCP(Br), there is no coupling of adjacent chains by hydrogen bonding, (ii) the degree of partial oxidation (0.40) is much larger than the characteristic one for KCP(Br) (0.30) implying a stronger Pt-Pt bonding, and (iii) the presumed linear bifluoride anions  $(\text{FHF})^-$  could produce a different random potential along the Pt chains.

For the interpretation of the nuclear- and electron spin relaxation data in KCP(Br), a variety of theoretical models have been proposed so far. It has been shown that some of the relaxation and lineshape phenomena observed by  $^{195}\text{Pt}$  NMR in KCP(Br) may be caused either by spin-carrying solitons via hyperfine interaction, or by spinless solitons via quadrupolar and chemical-shift interactions [1]. We have analysed the temperature dependence of the EPR linewidth in KCP(Br) in terms of motionally narrowed hyperfine interaction of an unpaired spin soliton delocalized over several platinum nuclei [2]. On the other hand, the results obtained by X-band EPR measurements, were interpreted as a superposition of the spin-phonon and spin-spin relaxation components in Q1D, within the framework of the mixed valence model [3]. Here, the motion of individual electrons along the chains was considered responsible for relaxation instead that of collective modes, like CDW's and solitons. Although the temperature and angular dependencies of the EPR linewidth fit well with the mixed valence model, this cannot be taken as a clear indication of its validity, since such a coincidence could also arise due to the large numbers of adjustable parameters introduced by this phenomenological model.

---

\* Paper presented at Romanian Conference on Advanced Materials, Bucharest, Romania, October 23-25, 2000

## 2. Experimental

Using our recent multi-frequency EPR measurements on RbCP(FHF) single crystals at 9.3 GHz (X-band), 35 GHz (Q-band) and 93 GHz (W-band), we show that, from simply analyzing the anisotropy of the spin-spin relaxation rate,  $(T_2)^{-1}$ , one can get important information concerning the nature of the electron spin excitations, and the relaxation mechanisms, in Q1D Pt-compounds. As the main motivation for our investigation, in the Fig.1 are illustrated the temperature dependencies of  $(T_2)^{-1}$ , for the parallel and perpendicular orientations of the static magnetic field with respect to the crystallographic  $c$ -axis, i.e., the Pt-chain axis. The results at X-band (Fig.1a) are similar to those reported in Ref.[2], and thus can be well explained within the mixed valence model, where the linewidth in the parallel case is always larger than in the perpendicular one. Inspecting the Fig.1b, however, one can see that exactly the opposite applies for the W-band data. The same behaviour was also obtained in Q-band. This suggests that another theoretical model, which contains an explicit frequency dependence of the relaxation parameters, is needed in order to explain the observed features.

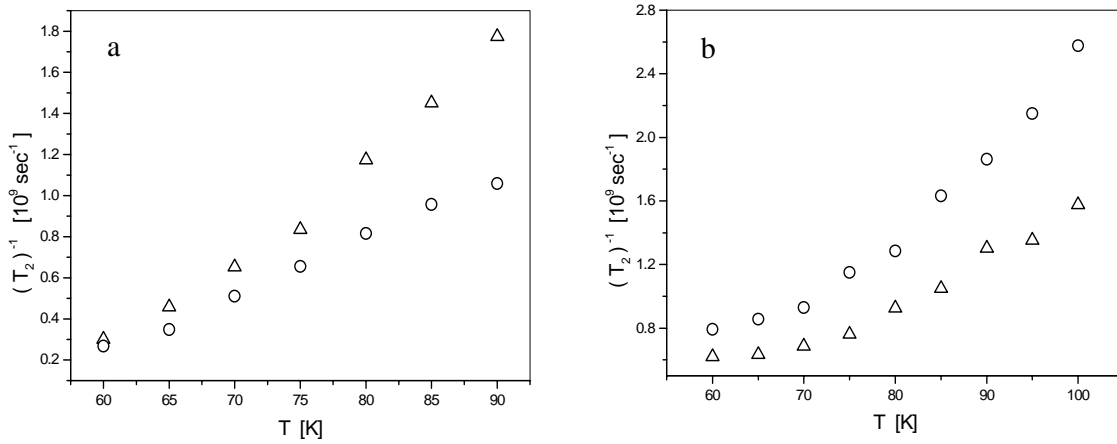


Fig. 1. The temperature dependencies of  $(T_2)^{-1}$  measured by EPR at: (a) 9.3 GHz (X-band), and (b) 93 GHz (W-band), for the parallel ( $\Delta$ ) and perpendicular ( $\circ$ ) orientation of the magnetic field with respect to the Pt – chain axis.

## 3. Results and discussion

The relaxation of the electron spin excitations is considered to be determined by the local dipolar- and hyperfine field fluctuations. Their contributions to the resultant spin-spin relaxation rate,  $(T_2)^{-1}$ , are given by

$$(T_2)_d^{-1} \propto C_d(T) \left[ (1 - 3 \cos^2 \theta)^2 J(0) + 10 \sin^2 \theta \cos^2 \theta J(\omega) + \sin^4 \theta J(2\omega) \right] \quad (1)$$

and

$$(T_2)_h^{-1} \propto C_h(T) \left[ 4(1 - 3 \cos^2 \theta)^2 + 18 \sin^2 \theta \cos^2 \theta \right] J(0) + \left[ (1 - 3 \cos^2 \theta)^2 + 36 \sin^2 \theta \cos^2 \theta + 9 \sin^4 \theta \right] J(\omega) \quad (2)$$

where  $C_d(T)$  and  $C_h(T)$  are weighting factors whose values depend on the relative strengths between the two coupling mechanisms,  $J(\omega)$  represents the spectral density function at the specified frequency, and  $\theta$  is the angle between the static magnetic field and the chain axis. The above relationships

indicate that, from an angular dependence of  $(T_2)^{-1}$  taken at a fixed temperature, one can get information about the relative values of spectral density functions and thus, implicitly, about the nature of the thermal motions of the spin excitations.

For this, however, one has to know the values of the coefficients  $C_d(T)$  and  $C_h(T)$ . In other words, a prior knowledge about the contributions to the  $(T_2)^{-1}$  of the two relaxation mechanisms, and their corresponding temperature dependencies, are needed. On the other hand, as was mentioned above, in the case of Q1D Pt-compounds, this issue is still a matter of controversy.

Therefore, for simplicity we consider in the following two separate cases. First, assuming that the dipolar mechanism dominates the relaxation, we fitted with the Eq. (1) the measured angular dependencies  $(T_2)^{-1}(\theta)$  for both, Q- and W-band data, taken at  $T = 70$  K. The corresponding fit parameters are consistent with the following ratios of the spectral density functions:  $J(0):J(\omega):J(2\omega) = 1:0.8:4$ , and  $J(0):J(\omega):J(2\omega) = 1:3:21$  for  $\omega = 35$  GHz and 93 GHz, respectively. A similar procedure was applied next, however, assuming now that the relaxation is dominated by the hyperfine mechanism. The experimental curves were fitted this time with the Eq. (2), and the corresponding results are consistent with  $J(0):J(\omega) = 1:4$ , for  $\omega = 35$  GHz, and  $J(0):J(\omega) = 1:3$  for  $\omega = 93$  GHz.

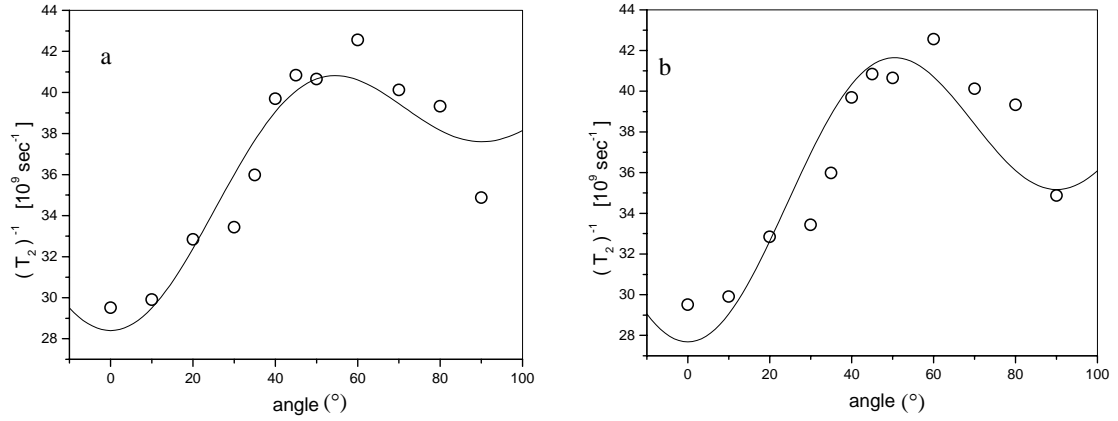


Fig. 2. The fits of the angular dependence of  $(T_2)^{-1}$  measured at 34 GHz (Q-band) with: (a) the Eq.(1), and (b) the Eq.(2).

To exemplify, in the Figs. 2a and 2b are shown the fits of the Q-band data with the Eq. (1) and (2), respectively. As can be seen from these figures, both functions can explain well the observed anisotropy. Therefore, these fittings cannot be taken as a clear indication of which relaxation mechanism dominates, or if they are of comparable magnitudes. To remove this ambiguity, one can use instead the results obtained from the fits, namely, the frequency dependencies of the spectral density functions. As can be seen from the Fig. 3a, a continuous increase with  $\omega$  of the  $J(\omega)$  was obtained for the dipolar relaxation mechanism, while, assuming a hyperfine mechanism, one can draw the conclusion that  $J(\omega)$  must show a maximum somewhere between 35 and 93 GHz (Fig. 3b).

If only a diffusion motion of the electron spins along the chain is assumed, the corresponding spectral density,  $J(\omega) = 2\tau/(1+\omega^2\tau^2)$ , is a continuously decreasing function of  $\omega$ . Obviously, another relaxation mechanism should also be present into the system, such as to determine the observed increase of the  $J(\omega)$  at high frequencies. On the other hand, from physical reasons,  $J(\omega)$  cannot increase indefinitely with  $\omega$ , but rather should behave like a function which is peaked around a certain frequency,  $\omega_0$ .

This particular form of the spectral density function is consistent with the soliton model. The strongest argument in favor of such an interpretation is, that the pinning frequency,  $\omega_F$ , of the CDW's along the chain was also found to be of the order of tenths of GHz [4]. Since, due to thermal motion, a Gaussian distribution of this frequency is likely to exist, it will give rise to random local field fluctuations at the solitons positions. Preliminary theoretical investigations have shown, that the above described mechanism will determine a resultant spectral density function whose shape at high-

frequencies is also a Gaussian, centered around  $\omega_F$ . Obviously, the interpretation of the experimental angular dependence of  $(T_2)^{-1}$  fits very well within this picture [5].

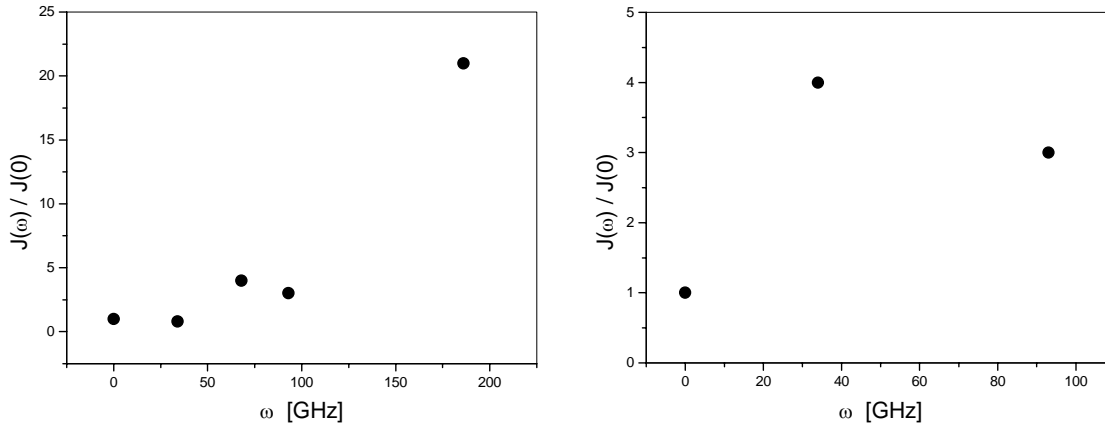


Fig. 3. The normalized spectral density function,  $J(\omega) / J(0)$ , evaluated considering a dominant (a) – dipolar, and (b) - hyperfine, relaxation mechanism.

The results corresponding to the dipolar relaxation indicate that  $\omega_0 > 186$  GHz (Fig.3a). Assuming a hyperfine mechanism, one obtained  $93 \text{ GHz} > \omega_0 > 35 \text{ GHz}$ . Relating this special frequency,  $\omega_0$ , where the experimental spectral density function shows a peak, with the CDW pinning frequency,  $\omega_F$ , obviously, the latter case corresponds better to the reported values of the  $\omega_F$  in KCP(Br) [4]. This suggest that, even if a dipolar interaction between solitons exists, it is dominated by the much stronger hyperfine coupling with the  $^{195}\text{Pt}$  nuclei [2].

#### 4. Conclusions

We have performed multi-frequency EPR investigations on the Rb(FHF) Q1D molecular conductor. While the temperature and angular dependencies of the EPR linewidth at X-band are consistent with the previously developed mixed valence model, strong deviations were obtained for the angular dependence obtained at Q and W-bands. The results of our investigations indicate that the electron spin excitations in Pt-Q1D conductors are represented by spin carrying solitons whose relaxation is dominated by the hyperfine mechanism.

#### References

- [1] M. Mehring, O. Kanert, M. Mali, D. Brinkmann, Solid State Comm. **33**, 225; M. Mehring in: Proc. 7-th AMPERE Summer School, Portoroz, Ed. R. Blinc, Slovenia, p.211, 199 (1980).
- [2] O. Pana, C. Kessler, C. Filip, L. V. Giurgiu, I. Ursu, M. Mehring, Appl. Magn. Reson. **12**, 247 (1997).
- [3] T. Takahashi, H. Doi, H. Nagasawa, J. Phys. Soc. Jpn. **48**, 423 (1980).
- [4] D. Brinkmann, O. Kanert, Nuclear Spectroscopy on CDW Systems, Ed. T. Bulz, Elsevier (1992).
- [5] L. V. Giurgiu, X. Filip, O. Pana, C. Filip, A. Darabont, R. Ordean, S. Knorr, J. Rahmer, M. Mehring, Proc. 30-th Congress AMPERE, Lisbon, Ed. A.F. Martins, Universidade Nova de Lisboa, Lisbon, Portugal, p. 21, 2000.