Electrical and magnetic properties of LiPc and LiPcI

M. Dumm, R. Spitzfaden, Peter Lunkenheimer, Martin Dressel, Alois Loidl, B. Aβmann, H. Homborg, P. Fulde

Angaben zur Veröffentlichung / Publication details:

Dumm, M., R. Spitzfaden, Peter Lunkenheimer, Martin Dressel, Alois Loidl, B. Aβmann, H. Homborg, and P. Fulde. 1997. "Electrical and magnetic properties of LiPc and LiPcI." *Synthetic Metals* 84 (1-3): 925–26. https://doi.org/10.1016/s0379-6779(96)04213-0.

Electrical and Magnetic Properties of LiPc and LiPcI

M. Dumm[a], R. Spitzfaden[a], P. Lunkenheimer[a], M. Dressel[a], A. Loidl[a], B. Aßmann[b], H. Homborg[b], and P. Fulde[c]

[a] *Institut für Festkörperphysik, Technische Hochschule Darmstadt, D-64289 Darmstadt, Germany*
[b] *Institut für anorganische Chemie, Christian-Albrechts-Universität, D-24098 Kiel, Germany*
[c] *Max-Planck-Institut für Physik komplexer Systeme, D-01187 Dresden, Germany*

Abstract

We studied the ac electrical (20 Hz $\leq \nu \leq$ 1GHz) and magnetic properties of the molecular semiconductors lithium phthalocyanine (LiPc) and lithium phthalocyanine iodide (LiPcI) at temperatures 1.5 K $\leq$ T $\leq$ 300 K. The frequency and temperature dependence of the complex ac conductivity suggest polarons as the dominant species of charge carriers. The higher conductivity of the iodine salt can be attributed to an enhanced mobility of the polaronic charge carriers due to a better overlap of the π-orbitals along the stacking direction of the molecules. Up to 300 K the dc conductivity can be described by $\sigma_{dc} \propto \exp(-(T_0/T)^{1/2})$, i. e. quasi one-dimensional tunneling of charge carriers is the dominant conduction process in both compounds. Preliminary electron spin resonance (ESR) experiments were performed on LiPc. A single narrow, lorentzian shaped line is observed. Below 30 K a significant decrease in linewidth appears which may indicate the onset of magnetic order or dimerization.

Introduction

Lithium phthalocyanines are the only nonoxidized monophthalocyanines with a relatively high conductivity in the semiconducting range [1]. The semiconducting properties of LiPc can be explaned by the formation of a Mott-Hubbard gap due to Coulomb repulsion of the unpaired electrons [2], which leads to a half filled conduction band [3]. The electrical conductivity of phthalocyanines can be enhanced over several orders of magnitude by doping with iodine.

The measurements of the transport properties of LiPc and LiPcI were carried out in a broad frequency range (20 Hz $\leq \nu \leq$ 1 GHz) [4]. Below 1 MHz we measured the complex conductivity $\sigma = \sigma' - i\sigma''$ using an autobalance bridge (HP 4284A). At higher frequencies (1 MHz $\leq \nu \leq$ 1 GHz) the conductivity was determined from the complex reflection coefficient of the sample located at the end of a coaxial line employing an impedance analyzer (HP 4191A). These experiments were performed in a ^{4}He bath cryostat at temperatures 1.5 K $\leq T \leq$ 300 K. To remove the absorbed oxygen, we applied for some hours a vacuum to the inner tube of the cryostat. The measurements of the magnetic properties were performed using a conventional ESR spectrometer working at 9.3 GHz (X-Band). For cooling the sample down to 4.2 K, we used a helium gas continuous flow cryostat.

AC Conductivity

In Fig. 1 we show the frequency dependence of real and imaginary part of the conductivity of LiPc. At low frequencies the data of σ' saturate while at higher frequencies

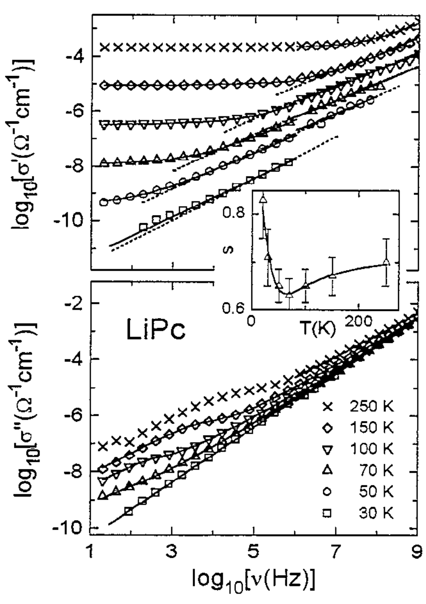

Fig. 1: Frequency dependence of real and imaginary part of the complex conductivity of LiPc for various temperatures. The solid lines are fits using $\sigma' = \sigma_{dc} + \sigma_0(\omega/\omega_0)^s$ and $\sigma'' = \tan(s\pi/2)\sigma_0(\omega/\omega_0)^s + \epsilon_0\epsilon_\infty\omega$ taking into account the contact contributions. The inset shows the temperature dependence of the frequency exponent s. Here the solid line is the result using OLPT model predictions. The dashed lines in $\sigma'(\nu)$ have been calculated according to the OLPT model predictions.

they follow a power law. Such a behavior is usually ascribed to charge transport by hopping processes and can be parametrized according to $\sigma' = \sigma_{dc} + \sigma_0(\omega/\omega_0)^s$ and $\sigma'' = \tan(s\pi/2)\sigma_0(\omega/\omega_0)^s + \epsilon_0\epsilon_\infty\omega$. Taking into account the contributions of the contacts between the samples and the gold contacts, $\sigma'(\nu)$ and $\sigma''(\nu)$ of LiPc and LiPcI were fitted simultaneously. The resulting temperature dependence of the frequency exponent s is plotted in the inset of Fig. 1 for LiPc. A distinct minimum in $s(T)$ indicates tunnelling of large polarons as dominant ac transport mechanism. The model of "overlapping large polaron tunnelling" (OLPT) makes predictions concerning the temperature and frequency dependence of the exponent s and the ac conductivity [5] which fit the observed $s(T)$ and $\sigma(T)$ behavior. As seen in the inset of Fig. 1 for LiPc a good agreement with the data can be achieved in both cases. The resulting fit parameters are $W_{H0} \approx 900$ K and $\alpha r_0 \approx 1.7$ for LiPc and $W_{H0} \approx 120$ K and $\alpha r_0 = 4.7$ for LiPcI. W_{H0} is the energie barrier height for infinite site seperation, r_0 the polaron radius and $1/\alpha$ is the spatial extent of the localized state wave function. The dashed lines in Fig. 1 show the frequency dependent ac conductivity calculated with the parameters mentioned above. They agree reasonably well with the measured data.

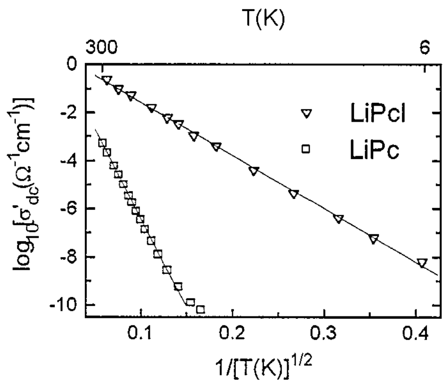

Fig. 2: Temperature dependence of σ_{dc} of LiPc and LiPcI. The solid lines are fits of Mott's VRH in one dimension.

From the dc-limit of the real part of the conductivity σ, the dc conductivity σ_{dc} can be evaluated taking into account the contact contributions. Fig. 2 shows the temperature dependence of σ_{dc}. Up to room temperature the data of LiPc and LiPcI can be fitted with $\sigma_{dc} = \sigma_0 \exp[-(T_0/T)^{1/2}]$ which indicates quasi one-dimensional variable range hopping (VRH) as dc transport mechanism [6].

Electron Spin Resonance

At elevated temperatures ($T = 250$ K) a single lorentzian line with $g = 2.0042$ and $\Delta H = 813$ mOe is observed in LiPc. These measurements are in agreement with measurements of Turek et al. [7]. With decreasing temperature the linewidth narrows almost linearly with a slope of 0.75 mOe/K (see Fig. 3). Below 30 K a drastic reduction in linewidth appears for further decreasing temperature. As seen in the inset, the intensity reveals a Curie-like increase for $T > 30$ K, and a significant decrease for lower temperatures. These anomalies could be explained by the appearence of magnetic order or dimerization of the spins of the paramagnetic centers. However, the decrease in linewidth is in contrast to former investigations [7]. The influence of residual absorbed oxygen cannot be excluded and more experimental data are needed to elucidate the origin of the anomalies.

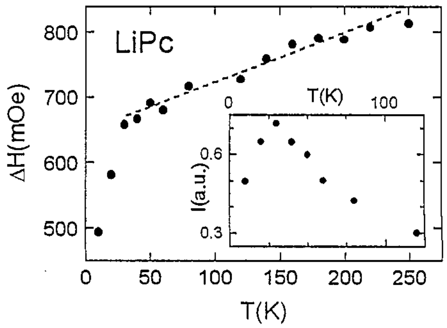

Fig. 3: Temperature dependence of the ESR linewidth ΔH and the intensity of the ESR signal (inset) of LiPc. The dashed line illustrates the linear narrowing of the linewidth with decreasing temperature ($T > 30$K).

Conclusion

We carried out measurements of the ac electrical and magnetic properties of LiPc and LiPcI. The frequency and temperature dependence of the complex conductivity of both materials can be explained assuming tunnelling of large polarons as dominant charge transport process. The smaller energy barrier W_{H0} in LiPcI is indicative of a better overlap of the π-orbitals in the tetragonal LiPcI compound as compared to the monoclinic LiPc and explains the higher conductivity in the former compound. We also determined the high frequency limit of the dielectric constant as $\epsilon_\infty \approx 6$ (LiPc) and $\epsilon_\infty \approx 20$ (LiPcI). The dc conductivity σ_{dc} exhibits a temperature dependence characteristic of quasi one-dimensional VRH. At room temperature the dc conductivities are $5.3 \times 10^{-4}\Omega^{-1}\text{cm}^{-1}$ (LiPc) and $0.2\ \Omega^{-1}\text{cm}^{-1}$ (LiPcI).

The ESR experiments indicate the onset of magnetic interactions below 30 K.

References

[1] P. Turek, P. Petit, J.-J. André, J. Simon, R. Even, B. Boudjema, G. Guillaud, and M. Maitrot, J. Am. Chem. Soc. 109, 5119 (1987)

[2] K. Yakushi, T. Ida, A. Ugawa, H. Yamakado, H. Ishii, and H. Kuroda, J. Phys. Chem. 95, 7636 (1991)

[3] E. Orti, J. L. Brédas, and C. Clarisse, J. Chem. Phys. 92, 1228 (1990)

[4] M. Dumm, P. Lunkenheimer, A. Loidl, B. Aßmann, H. Homborg, and P. Fulde, J. Chem. Phys. 104, 5048 (1996)

[5] A. R. Long, Adv. Phys. 31, 553 (1982)

[6] N. F. Mott and E. A. Davis, *Electronic Processes in Non-Crystalline Materials* (Oxford University, Oxford, 1979)

[7] P. Turek, J.-J. André, and J. Simon, Solid Stat. Commun. 63, 741 (1987)