Magnetic Properties of Lithium Phthalocyanine

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Abstract

The magnetic susceptibility and specific heat of the organic semiconductor lithium phthalocyanine (LiPc) are studied for temperatures 1.5 K $\leq T \leq$ 300 K. LiPc has one unpaired electron on the inner ring of the macrocycle. These electrons are localized along the molecular stack and behave like spin chains. The spin susceptibility, as determined by electron spin resonance measurements, and the magnetic contribution to the heat capacity are well described by a model of a S=1/2 antiferromagnetic Heisenberg chain. The exchange constant is given by $J \approx$ 40 K. In comparison the iodinated compound LiPcI is ESR silent. Due to oxidizing with iodine the unpaired electrons have been removed from the macrocycle.

The electron spin resonance measurements (ESR) were performed using a conventional ESR spectrometer at X-band frequencies for temperatures 1.5 K $\leq T \leq$ 300 K. To avoid effects of absorbed oxygen (see e.g. [1] and references therein), the powdered samples were exposed to high vacuum over a period of several days; the sample handling was done under argon atmosphere. The heat-capacity measurements were performed in a home-built adiabatic Nernst calorimeter operating between 2 and 100 K.

The observed ESR signal of LiPc consists of a single small resonance line. The signal is well fitted by a Lorentzian line with ΔH =700 mOe and a g-shift $\Delta g = -0.0003$ at room temperature. The temperature dependence of the ESR intensity which directly corresponds to the spin susceptibility is shown in Fig. 1. With decreasing temperature the intensity increases to a maximum at around 30 K and then falls to a finite value at low temperatures. This is a clear signature of a spin 1/2 antiferromagnetic (AFM) Heisenberg linear chain. Bonner and Fisher [2] studied the magnetic and thermal properties of a $S = 1/2$ AFM linear chain. For temperatures 10 K $\leq T \leq$ 300 K this model can satisfactorily be fitted to the ESR intensities. The AFM exchange constant is given by $J = 40$ K.

LiPcI reveals a weak ESR signal. It is smaller by a factor of 10 to 20 compared to the signal in LiPc but shows the same line shape and a similar temperature dependence. Hence, the observed ESR signal results from paramagnetic defect states (mostly LiPc residues). Thus it is obvious that pure LiPcI is ESR silent with no free radical electron.

Spin systems like LiPc have two contributions to the total heat capacity C, the lattice contribution C_l and the magnetic contribution C_m. After the determination of C_l as described elsewhere [3] we calculated C_m. The inset in Fig. 1 shows $C_m(T)$ between 10 K $\leq T \leq$ 25 K. Following Bonner and Fisher [2], at low temperatures C_m increases lineary with temperature, then rises to a maximum at $T/J = 0.48$, and finally decreases with increasing temperatures. The observed maximum at $T_{\max} \approx 18$ K corresponds to a next-nearest neighbor exchange $J \approx 38$ K. This result is in agreement with the result derived from the ESR measurements.

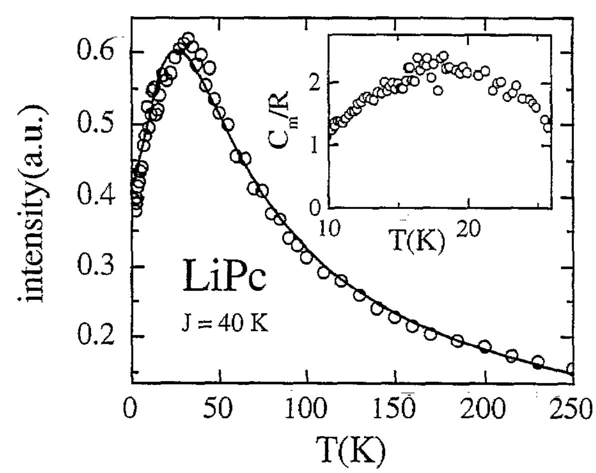

Fig. 1: Temperature dependence of the ESR intensity. The solid line is a fit using the Bonner-Fisher model for a $S = 1/2$ AFM linear chain with $J = 40$ K. The inset shows the magnetic contribution to the heat capacity C_m as a function of temperature.

A more extensive investigation of LiPc and the iodinated conpound LiPcI is found in [3]. We thank B.Aßmann and H. Homborg for providing the LiPc and LiPcI samples.

References

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[2] J. C. Bonner and M. E. Fisher, Phys. Rev. 135 (1964) A640.

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