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ESR-Experiments on the Radical Cation Salt $(Naphthalene)^{+}_{2}\,AsF^{-}_{6}$

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ESR-EXPERIMENTS ON THE RADICAL CATION SALT (NAPHTHALENE)$_2^+AsF_6^-$

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ESR- and DC-conductivity measurements on (Naphthalene)$_2$ AsF_6 show in metallic properties above 240 K with the narrowest ESR-line (ΔB_{pp} = 2,5 mG) found so far in solids. Below 240 K we have a semiconductor and at about 110 K a structural phase transition which leads to an enhancement of the ESR-linewidth by one order of magnitude.

INTRODUCTION

Radical cation salts, known since more than one decade[1] have aroused considerable attention due to a strong temperature dependence of their electrical and magnetic properties. These salts are metallic like at room temperature and semiconducting below a phase transition region[2]. Naphthalene$_2$ AsF_6, the system we are interested in, was first reported by Fritz et al.[3], who have investigated its crystal structure and have found ESR-linewidths[5] of about 0.1 Gauss at room temperature and 150 K.

After the first proof of extremely narrow ESR-lines at high temperatures(ΔB_{pp} = 2.5 milliGauss at 240 K) and the enhancement of the linewidth by two orders of magnitude at

about 110 K, we have performed ESR-experiments in the whole temperature range from 4 to 290 K. In the following we like to present the measurements of the ESR-linewidth, the ESR-intensity and preliminary DC-conductivity data and the discussion of these results by using a model of temperature dependent delocalization of paramagnetic species.

EXPERIMENTAL

The ESR-experiments have been performed with a conventional Varian X-Band ESR spectrometer (E-109) using a variable temperature helium cryostat (Oxford ESR-9) for the temperature dependent measurements.

The conductivity measurements used in the discussion were carried out at the set up of the Max Planck Institute/ Heidelberg, which is described elsewhere[2].

The crystals were grown by anodic oxidation at -40°C[3]. One obtains small black shiny needles and plates, respectively. The crystal structure[3] shows stacks of $(\text{Naphthalene})_2^+$-molecules which are well separated from each other leaving open channels for the AsF_6^--anions. The distance between the Naphthalene planes within the stack is very low (d = 3,18 Å).

EXPERIMENTAL RESULTS

Over the whole temperature range between 4 and 300 K one obtains only one extremely narrow Lorentzian shaped line near g = 2 which saturates at very low power levels (fig. 1 left).

Experimental problems occur if the linewidth is less than 20 mG, which happens at $T \geq 230$ K: due to apparatus difficulties the automatic frequency control (AFC) and the field modulation had to be switched off.

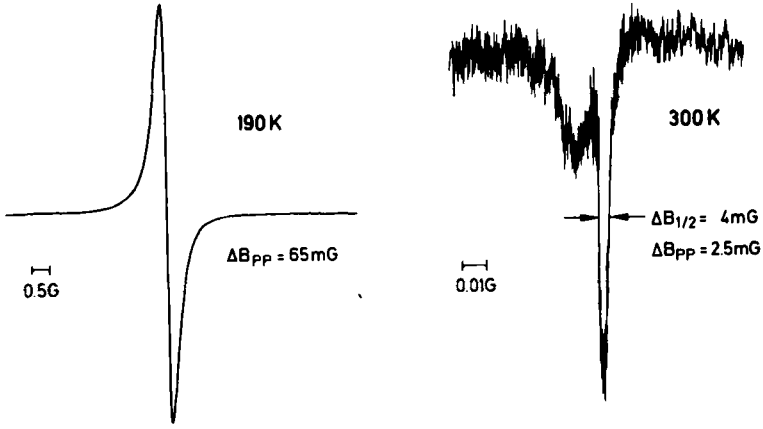

FIGURE 1 ESR-signals on Naphthalene$_2$AsF$_6$ at 190 K (left) and 300 K (right, without AFC and field modulation).

ΔB_{pp} as a function of the reciprocal temperature is given in the upper part of fig. 2. Starting with the lowest temperature, the linewidth decreases from ΔB_{pp} = 0.45 G at 4 K to 0.07 G between 50 K and 90 K. Further increase in temperature leads to a peak in the linewidth of 0.35 G at 110 K which is followed by a nearly continuous decrease up to 240 K where we reach the lowest value of the linewidth, which stays constant up to T = 300 K.

This high temperature value of the linewidth varies from 0.0025 to 0.04 G depending on the quality of the sample.

The ESR-signal-intensity (fig. 2 lower part) shows a Curie-like behaviour of the paramagnetic species at lower temperature and a thermally activated intensity (E ≅ 0.16 eV above 95 K. Between 110 and 155 K there is a plateau (a nearly temperature independent intensity) which coincides on the temperature scale with the maximum in the $\Delta B_{pp}(T)$-curve.

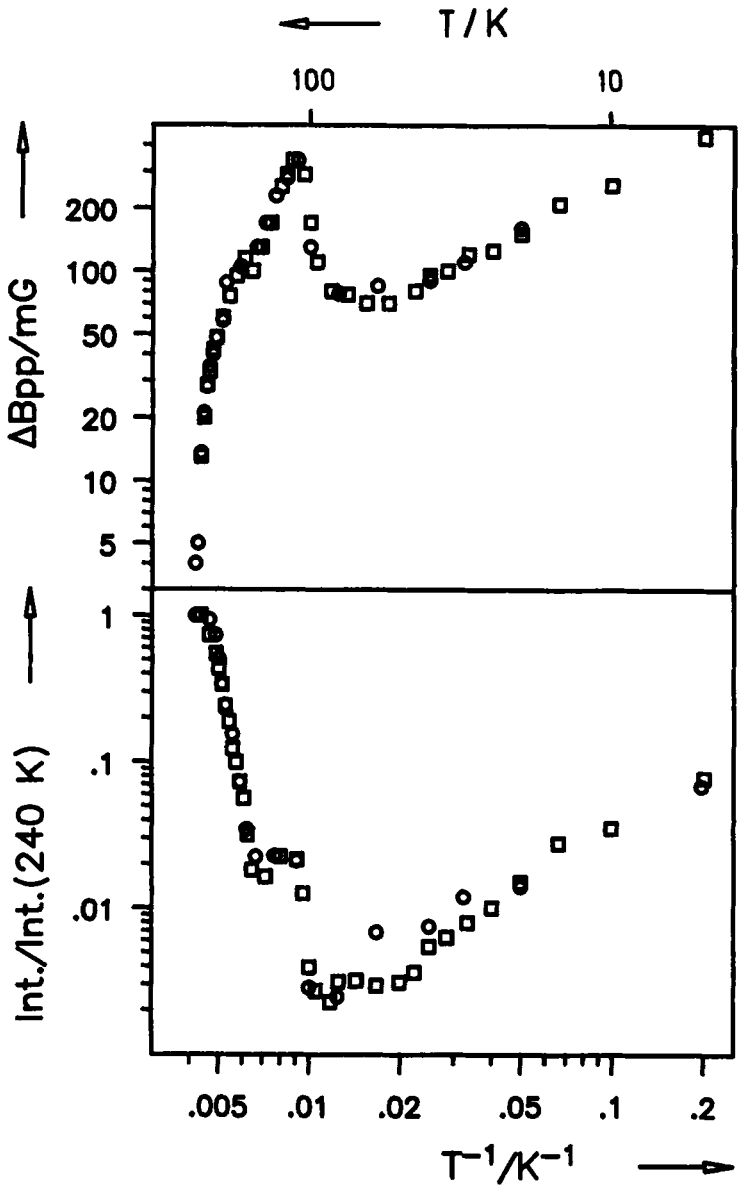

FIGURE 2 The ESR-linewidth ΔB_{pp} (upper part) and the ESR-intensity (lower part) as function of the reciprocal temperature in a double logarithmic scale. Different symbols mean different samples.

Above 240 K the ESR-intensity is constant with a corresponding suceptibility χ of about 4×10^{-5} cm^3/mole Naphthalene$_2$ AsF_6.

The g-factor is constant over the whole temperature range investigated so far within the experimental accuracy of $\pm$ 6 ppm. Its absolute value is about g = 2.0025.

Angular dependent measurements of the g-factor and the linewidth show an anisotropic behaviour of these properties.

A replacement of the AsF_6^--anions by PF_6^- does not change the ESR-results.

DISCUSSION

The narrow Lorentzian shaped ESR-line at g = 2.0025, which coincides with the g-value of the Naphthalene radical cation[4] points to a strong delocalization of s = 1/2-spins along the Naphthalene stacks.

In the following we distinguish between three temperature regions: the low temperature range, where we have a Curie like susceptibility, the range between 95 and 155 K which we believe is due to a phase transition and the range above 155 K, where a decreasing gap between the valence and conduction band drives the crystal from a semiconducting behaviour to that of an organic metal at $T \geq 240$ K.

At low temperature we assume an antiferromagnetic behaviour of the crystal, the residual spins being due to defects in the Naphthalene stacks, acting as shallow donors or acceptors.

The concentration of these spins is constant with temperature, the delocalization increasing with increasing temperature as indicated by the narrowing of the Lorentzian shaped lines.

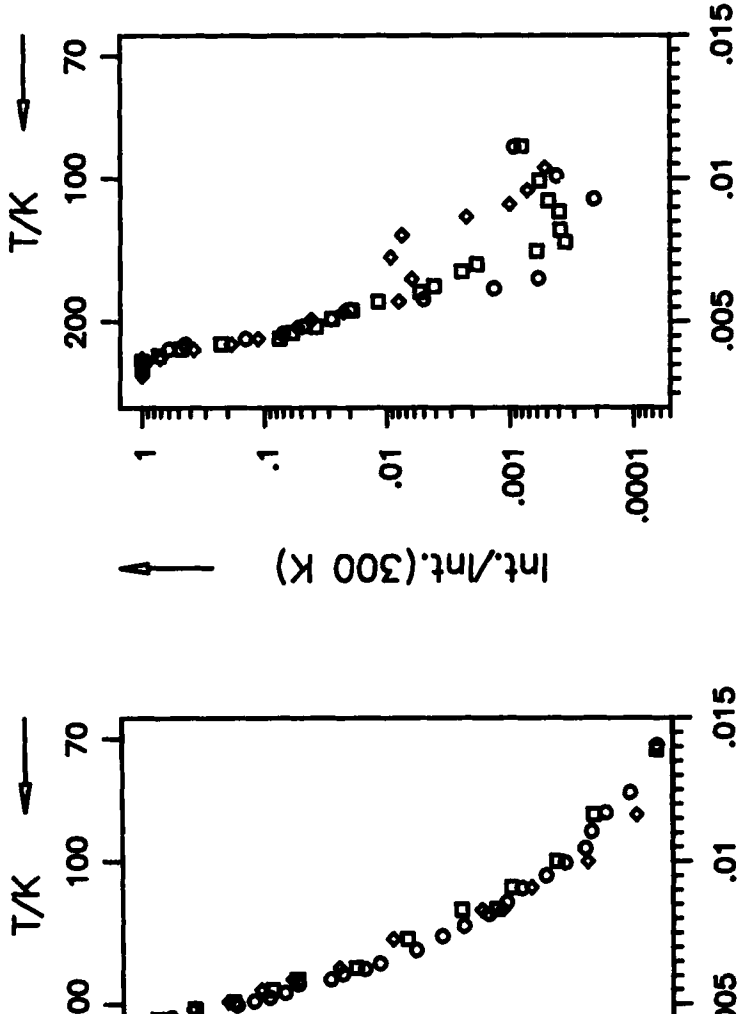

FIGURE 3 Comparison of the normlized DC-conductivity (left) and ESR-intensity (right).

In our model cooperative phenomena due to a phase transition begin to distort the antiferromagnetic order at about 95 K leading to shorter T_1 and T_2-values and an increase of the paramagnetic species as seen in the increasing ESR-linewidth and intensity. Above the phase transition the delocalization of the spins increases again (ΔB_{pp} decreases) with increasing frequencies of the soft modes.

The picture of a structural phase transition is supported by similar ESR-results on TMA-TCNQ-I[5] where the lattice distortion was proved directly by electron diffraction measurements[6].

The fading of the phase transition coincides with the onset of a thermal activation of the spins into the conduction band which is separated by 0.32 eV from the valence band as deduced from the slope of the ESR-intensity and the DC-conductivity in fig. 3.

This gap has to be temperature dependent. In a first approach we assume a linear decrease of the gap from 110 K towards zero at about 240 K. This statement is based on a continuous transition to the metallic state (fig. 3) and on a spin concentration of 2×10^{22}/mole in this region, which is in accordance with a susceptibility χ of about 4×10^{-5} cm^3/mole. Using a hyperfine interaction of 2.28 G for the $(Naphthalene)_2^+$-ion[8] means, that the spin is delocalized over 2.5×10^5 Naphthalene molecules. Here we reach macroscopic distances in a one dimensional picture.

The comparison of the ESR-intensity and the DC-conductivity confirm our model of a semiconductor above 155 K, and of a transition to the metallic state above 240 K (Pauli-susceptibility and nearly temperature independent conductivity) as found in similar compounds[9].

It should be mentioned - so far unexplained - that the phase transition at 110 K which dominates in most samples the properties of our paramagnetic species does not show up in the DC-conductivity.

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