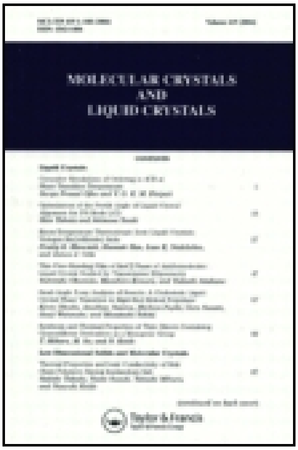

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Pressure Effect on MTPP $(TCNQ)_2$ And MTPA $(TCNQ)_2$ Salts Studied by Electron Spin Resonance

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PRESSURE EFFECT ON MTPP$(TCNQ)_2$ AND MTPA$(TCNQ)_2$ SALTS STUDIED BY ELECTRON SPIN RESONANCE

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Abstract ESR pressure studies of MTPP$(TCNQ)_2$ and MTPA$(TCNQ)_2$ were performed. The p-T phase diagram was described.

INTRODUCTION

In this paper we present the ESR pressure studies of the ion-radical salts of TCNQ with methyltriphenylphosphonium (MTPP$(TCNQ)_2$) and methyltriphenylarsonium (MTPA$(TCNQ)_2$). We pay our attention on pressure dependence of the phase transition temperature. It is well known[1] that MTPP$(TCNQ)_2$ undergoes a first-order structural phase transition at normal pressure at 315.7 K, whereas the similar salt MTPA$(TCNQ)_2$ undergoes only the pressure-induced phase transition.[1-4]

EXPERIMENTAL AND RESULTS

We performed the ESR measurements of oriented single crystals of MTPP$(TCNQ)_2$ and MTPA$(TCNQ)_2$, using the X-band microwave spectrometer equiped with special pressure and temperature appliances.

The line evolutions for two perpendicular orientations of MTPP$(TCNQ)_2$, at normal pressure, together with the line evolution of MTPA(TCNQ)$_2$ are shown in Fig.1.

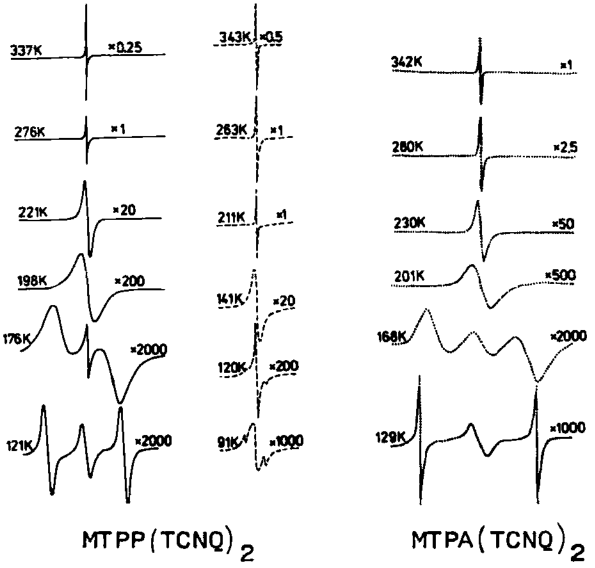

FIGURE 1 The line evolutions for the salts, at normal pressure.

At high temperatures, single lines of both crystals are sharp, about 0,07 mT in width and Lorentzian in shape. With the decreasing temperature the lines broaden slowly; at the transition of MTPP(TCNQ)$_2$ it broadens considerably and suddenly. Below the phase transition T, the single line broadens on, deforms and then splits. The doublet components become progressively sharper with the decreasing temperature.

The linewidth for the single lines of MTPP(TCNQ)$_2$ and MTPA(TCNQ)$_2$ plotted against p, for selected temperatures is shown in Fig.2. The linewidthes of both crystals display hysteresis, typical for the first order phase transitions. The pressure dependent hysteresis broadens with the decreasing pressure.

FIGURE **2**

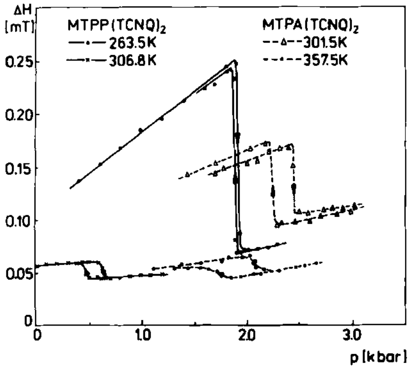

FIGURE 3

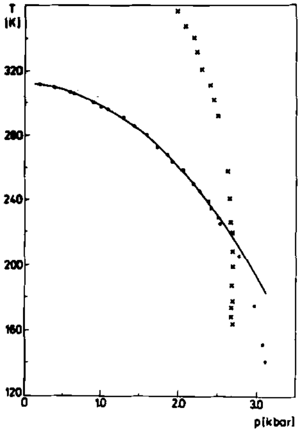

FIGURE 2 The linewidth of the salts vs. pressure.

FIGURE 3 The p-T phase diagrams of the salts • $MTPP(TCNQ)_2$, x $MTPA(TCNQ)_2$.

DISCUSSION

Our studies confirm the phase diagrams for both salts given by Merkl et al.[1] They fitted the experimental phase diagrams to an equation ensued from a model of noninteracting triplet excitons. His model is based on oversimplificated assumptions, and should be reexamined.

Instead of this approach we propose a model of interacting triplet excitons in a compressible solid. We consider the entropy of transition as a sum of a spin entropy change ΔS_{spin} and a configurational entropy, describing mainly the reorientation of two phenyl groups (ΔS_{orient}):

$$\Delta S = \Delta S_{spin} + \Delta S_{orient}$$

According to Chesnut et al.[5] :

$$\Delta S_{spin} = R\,(\rho_{II} - \rho_{I})\ \ln g$$

where ρ_I and ρ_{II} are the excitation densities in the high and low temperature phases, respectively; R and g are constants.

Taking into account the volume change at phase transition $\gamma \equiv \Delta V/V_0$ and the compressibility of crystal, we have a modified Bridgman equation:

$$p \Delta V = \gamma V_0 \left(p - K p^2 + \beta p^3\right)$$

where K and β are linear and nonlinear compressibilities of the crystal.

The above equations lead to the following formula:

$$T_p = \frac{\Delta E' + \gamma V \left(p - K p^2 + \beta p^3\right)}{\Delta S_{orient} + R\left(\rho_{II} - \rho_I\right) \ln 3 + k\ n\ \ln\left[(1-\rho_I)/(1-\rho_{II})\right]}$$

describing the p-T phase separation curve in the case of compressible organic solid with interacting triplet excitons.

The comparison between the experimental data and the theory with the only one adjustable parameter $\Delta E'$ for MTPP(TCNQ)$_2$ is shown in Fig.3.

Nonlinear compressibility as well as nonlinear contribution to the cooperative attractive interaction between excitons are probably responsible for deviation from our model observed at higher pressure.

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