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The electronic properties of a radical cation salt of bis-ethylenedioxodibenzofuran, \([(\text{bEDODBF})_5(\text{AsF}_6)_2(\text{CH}_2\text{Cl}_2)_{0.2}]\)

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Résumé. — Les cristaux donnés dans le titre montrent un comportement semi-conducteur avec \(\sigma (300 \text{ K}) \approx 10^{-3} (\Omega \text{ cm})^{-1}\). La conductivité résulte de l'activation thermique d'électrons provenant de défauts dans la bande interdite vers la bande de conduction. Cependant, la susceptibilité est grande \(\chi (300 \text{ K}) = 5 \times 10^{-4} \text{ emu/mole et de type Pauli pour } T > 50 \text{ K et non corrélé à la conductivité. La localisation des électrons dans un ordre antiferromagnétique est prouvée par la dépendance angulaire de la largeur de la raie de résonance de spin électronique. Cette dépendance angulaire correspond à une interaction dipole-dipole dans la limite d'échange intermédiaire avec une diffusion de spin à une dimension.}

Abstract. — Crystals of the title compound show a semiconducting behaviour with \(\sigma (300 \text{ K}) \approx 10^{-3} (\Omega \text{ cm})^{-1}\). The conductivity results from thermal activation of electrons from defect states in the band gap into the empty conduction band. The susceptibility, however, is large \(\chi (300 \text{ K}) = 5 \times 10^{-4} \text{ emu/mole and Pauli-like at } T > 50 \text{ K and not correlated to the conductivity. The location of the electrons in an antiferromagnetic order is proven by the angular dependence of the ESR linewidth. This angular dependence corresponds to dipole-dipole interaction in the intermediate exchange limit with one-dimensional spin diffusion.}

1. Introduction.

Radical cation salts, rcs, have recently attracted a considerable interest since their reduced dimensionality gives rise to many interesting physical properties, such as extremely narrow magnetic resonance lines [1] and quasi one- (two-) dimensional charge transport along stacks (in planes) of aromatic molecules [2].

In our study of the electronic properties of new radical cation systems and their chemical stability, we have focused on organic donors based on alkylated dibenzofuranes [3, 4]. In this communication the synthesis and the electronic properties of the donor bis-ethylenedioxydibenzofuran with hexafluoroarsenate as anion, \((\text{bEDODBF})_5(\text{AsF}_6)_2(\text{CH}_2\text{Cl}_2)_{0.2}\), are presented.

2. Synthesis.

2,3,6,7-bis-EthyleneDiOxoDiBenzoFuran,
bEDODBF, is conveniently prepared by alkylation of 2,3,6,7-tetrahydroxydibenzofuran [5] in DMSO with sodium carbonate as base.

A typical procedure is as follows : to a solution of 14 g of 1,2-dibromoethane and 4.29 g crude \(\mathbf{1}\) in 150 mL dry DMSO under \(\mathbf{N}_2\), 11.75 g of sodium carbonate is added, and the mixture is warmed to 325 K during 3 days. Standard procedure work-up followed by column chromatography, in a hexanes/toluene gradient, gave 1.82 g of bEDO BF...
The resulting crystals had a mp of 481-483 K. Further purification by recrystallization from ethanol and gradient sublimation gave pure 2 with mp 487 K [6]. Cyclovoltammetry of 3 mM bEDODBF in dichloromethane containing 0.15 M (nBu)4NAsF6, with a scan rate of 100 mV/s, revealed a quasi-reversible peak at 1.30 V vs. SCE. Constant current electrolysis, 4.5 µA/cm², of bEDODBF in 0.05 M (nBu)4NAsF6 yielded the radical cation salt as beautiful black glimmering nets, growing perpendicular from the electrode. Visible absorption spectra of the mother liquor of the electrolysis showed a maximum at 698 nm and a shoulder at 674 nm. Elemental analysis gave the composition of the rcs as (bEDODBF)₃(AsF₆)ₓ(CH₂Cl₂)₁₋ₓ.

An X-ray investigation gave evidence that the bEDODBF/AsF₆ crystals were disordered [7]. The disorder is probably caused by the incorporated solvent, CH₂Cl₂, used in the electrocrystallization of the rcs.

3. Experimental.

For details about the conductivity measurements and the ESR experiments see reference [4]. The absorption measurements were made with a FTIR spectrometer in the wavelength range 400 to 4 000 cm⁻¹ with a resolution of 4 cm⁻¹. The measurements were performed on composite samples of KBr and bEDODBF/AsF₆ (bEDODBF), with a volume fraction of bEDODBF/AsF₆ (bEDODBF) of 1.5 x 10⁻³. The samples were prepared by mixing the KBr powder and the powder from ground single crystals, the mixture was then pressed into a pellet. The small suspended sample particles can thus be treated as isolated particles in the insulating and transparent KBr matrix. With a pellet of the host KBr in the reference path of the spectrometer the absorption coefficient could be determined.

4. Results.

4.1 ABSORPTION. — The absorption spectrum of the donor, bEDODBF (Fig. 1) and the rcs, bEDODBF/AsF₆, (Fig. 2) consists of many vibrational bands between 400 and 1 600 cm⁻¹, mainly from different vibrational modes of the aromatic bEDODBF molecule. In the latter case the vibronic features are rather blurred. The spectrum of the donor is almost flat above 1 600 cm⁻¹ with \( \alpha \approx 0.7 \times 10^3 \) cm⁻¹. The main vibronic features seen in this frequency range are; C-H stretches from the sidegroups (around 3 000 cm⁻¹) and the aromatic C-H stretch (3 050 cm⁻¹). The broad peak in the absorption around 3 400 cm⁻¹ originates from H₂O in the KBr. The spectrum of the rcs shows a different behaviour; the absorption increases from \( \alpha \approx 4.1 \times 10^3 \) cm⁻¹ at 1 600 cm⁻¹ to \( \alpha_{\text{max}} \approx 7 \times 10^3 \) cm⁻¹ at about 3 400 cm⁻¹. At higher frequencies the absorption decreases slowly to 6.8 x 10³ cm⁻¹ at 4 000 cm⁻¹.

4.2 CONDUCTIVITY. — Measurements of the conductivity along the needle axis of bEDODBF/AsF₆ gave a room temperature conductivity of \( \sigma_{\text{RT}} = 1 - 3 \times 10^{-3} \) (Ω cm)⁻¹. The conductivity was activated with \( \Delta H = 119 \pm 11 \) meV at high temperatures. The activation energy changed around 175 K to \( \Delta_1 = 43 \pm 2 \) meV (Fig. 3).

A few of the investigated samples, from two different batches, showed a different temperature behaviour of the conductivity. They had a constant activation energy of about 45 meV from 300 K down to 220 K, where all samples showing this temperature dependence broke. The room temperature conductivity was more than one order of magnitude lower for these samples, \( \approx 10^{-4} \) (Ω cm)⁻¹.

4.3 ELECTRON SPIN RESONANCE. — By comparison of the signal intensity of the homogeneously broadened ESR signal with a calibrated sample the paramagnetic susceptibility was obtained, \( \chi (300 \text{ K}) = 5 \times 10^{-4} \) emu/mole. This value is high and almost constant between 300 and 150 K. The susceptibility decreases below 150 K and has a
5. Discussion.

At first glance, there seems to be a contradiction between the results of the ESR experiment and the conductivity measurements: A high Pauli-like sus-
ceptibility and a narrow ESR line point towards a metallic behaviour and extended electron states, while the thermally activated conductivity points to a semiconductor-like behaviour. Nevertheless, taking into account the broken stoichiometry, a model can be proposed which explains the electronic properties of bEDODBF/AsF$_6$. This model is based on the fact that bEDODBF/AsF$_6$ is a quasi one-dimensional solid with segregated stacks. This assumption is based on the temperature dependence of the susceptibility (see below) and the knowledge that this kind of molecules upon electrocrystallization tend to form salts with segregated stacks which are quasi one-dimensional. From the 5:2 stoichiometry of the rcs and the large electron-electron repulsion present, as deduced from the high susceptibility, one obtains the Fermi wave vector $k_F = \frac{2 \pi}{5a}$, where $a$ is the intermolecular distance in the regular cation stack. Anions regularly spaced ($\Lambda = 2.5a$) give rise to a potential with $q = \frac{4 \pi}{5a} = 2k_F$. This potential creates a band gap at $k_F$ since any perturbation (that couples to the electrons) with $q = 2k_F$ will open a band gap at the Fermi level in one dimension [8].

The proposed model therefore consists of a full band separated from an empty one by a band gap, $\Delta E$, appearing at $k = \frac{2 \pi}{5a}$. In the band gap there are defect levels. These states are generated by the disorder present.

A rough estimate of the size of the band gap can be obtained from the absorption measurements. Comparing the absorption spectra of the donor (Fig. 1) and the rcs (Fig. 2) one finds that the absorption coefficient of the rcs increases rather rapidly above $1\,650\,\text{cm}^{-1}$, in contrast to the donor that has an almost constant absorption coefficient in this energy range. The increase in the absorption of the rcs is due to electronic contributions from the mixed valence state of the bEDODBF molecules in the rcs. The additional absorption is caused by a CT-excitation, either an intermolecular charge transfer or the formation of a bound electron-hole pair state (local CT). Both kinds of CT-excitation should have an energy less than $\Delta E$ because these excitations do not have to overcome the large electron-electron repulsion between two electrons on the same molecule [9, 10]. The energy of the maximum of $\alpha_{\text{esr}}$ gives $\Delta E_{\text{CT}} \approx 0.4\,\text{eV} < \Delta E$. Since the activation energy deduced from the bi-exponential, in some cases exponential, decay of the conductivity with decreasing temperature $\Delta H$ or $\Delta L$, at high temperatures, is much smaller than $\frac{1}{2}\Delta E_{\text{CT}}$, the thermally activated conductivity must be caused by thermal excitations of electrons from the valence band to defect states in the gap or from defect states in the gap to the conduction band. Attempts to fit the conductivity data to different models of phonon-assisted hopping of electrons among located states near the Fermi level [11, 12], usually applied to disordered materials with located electrons, gave no satisfactory fit to the experimental data. Furthermore, with a typical phonon frequency of about $10^{12}\,\text{Hz}$ the decay length of the electron state was found to be $\ll 1\,\text{Å}$ for the one-, two- and three-dimensional variable-range hopping models. These values are in all cases too small to explain the measured value of the conductivity. All these models have in common that $N(E_F) \neq 0$, where $N(E_F)$ is the density of states at the Fermi level. This finding gives further evidence for a band gap at $E_F$.

The two different behaviours of $\sigma(T)$ found are consistent with defect states in the band gap. The crystals with a change from $\Delta H$ to $\Delta L$ at $175\,\text{K}$ have (at least) two different defect levels in the gap, and the crystals with only one activation energy, $\Delta L$, only one. The defect level with $\Delta L$ has the same value of $\sigma_0$ in both kinds of crystals, where $\sigma_0$ is the constant pre-exponential factor in $\sigma(T) = \sigma_0 \exp(-\Delta E/kT)$, indicating that the number of defect states of this kind is the same in all crystals. The value of $\sigma_0$ is about 0.2 $(\Omega \text{cm})^{-1}$, this value being much smaller than what is known from quasi one-dimensional metals which have $\sigma_0 \approx 100\,\text{cm}^{-1}$. Therefore, we believe that the concentration of charge carriers (defect states) is at most in the order of $0.002/\text{mole}$. Correlation of the states with the structural disorder is not possible yet.

For the interpretation of the magnitude and temperature dependence of the ESR intensity we follow the model of full bands (located spins) with strong electron-electron repulsion. There is one electron per site and we have a Mott-Hubbard insulator. Spin pairing is possible but not necessary. One-dimensional antiferromagnetic ordering with exchange coupling $J$ (according to the Bonner-Fisher model [13]) takes place. A coupling constant of $J = 300\,\text{K}$ fits the magnitude and the temperature dependence of the susceptibility between 300 and $150\,\text{K}$ rather well. The rather strong decrease in $\chi$ below $150\,\text{K}$ can be attributed to a further spin pairing associated with a structural phase transition favouring a dimerization. At temperatures below $40\,\text{K}$ the susceptibility follows $T^{-\alpha}$ law with $\alpha < 1$. A temperature dependence of this kind is characteristic of a one-dimensional random exchange Heisenberg antiferromagnetic chain (REHAC) [14, 15]. In this model, which is an extension of the antiferromagnetic Heisenberg chain with uniform exchanges, some disorder present gives rise to a distribution of the exchange interaction. The divergence of $\chi$ at low temperatures indicates that the weak exchange $\epsilon J$ which are present in this model among uniform exchanges $J$ become important in this temperature regime [14, 15, 16], i.e. $kT \gg \epsilon J$. 


A rough estimate of the defect concentration can also be obtained from the ESR intensity at low temperatures. At 20 K the intensity is as large as that at 300 K which corresponds to a spin concentration of 0.3/molecular unit. Therefore, the concentration of spins (defects) is approximately 0.02/molecular unit at 20 K. This estimate is based on a Curie-law behaviour. However, the intensity follows a $T^{-a}$ law with $a \approx 1$ below 40 K, clearly indicating that coupling of the spins takes place [14] even at low temperatures. This temperature dependence of the susceptibility at low temperatures implies that even more defects are present than estimated above. But these states may only participate partially as electronic states interacting with the conduction band by thermal activation.

The assumption of a phase transition at 150 K is supported by the increase in the ESR linewidth close to that temperature: Increasing amplitudes of soft modes, when the temperature is approaching $T_c$, may slow down the spin diffusion and therefore the averaging of the dipolar spin-spin interaction. Below the phase transition the linewidth starts to decrease again since the relaxation rate again begins to decrease monotonously. This behaviour persists down to 40 K where the weak exchanges [14, 15, 16] become important. At low temperatures the weak exchanges cause the antiferromagnetic chain segments with $S = 0$ to be longer which in turn decreases the exchange frequency and thereby the linewidth increases [14, 16].

The dominance of the dipolar spin-spin interaction on the ESR linewidth is clearly seen in the angular dependence of $\Delta B_{pp}$. There is no coincidence with the angular dependence of the spin-orbit coupling, SOC, as in the case of mobile spins. A measure for the strength of the SOC is the deviation of the experimentally determined $g$-factor, $g_{exp}$, from that of the free electron value. In the case of SOC $\Delta B_{pp}$ is proportional to $\Delta g^2/\tau$, with $\tau$ being the scattering time [17].

As seen from figure 5 there is no correlation of this kind between $\Delta B_{pp}$ and the $g$-factor. The lack of any influence of SOC on the linewidth is a strong support for the model of located electrons in bEDODBF/AsF$_6$.

A quantitative fit to the ESR linewidth as a function of $\Theta$ is achieved by the following model:

- There are located electron states.
- Their spins interact via dipolar interaction with each other.
- This interaction is time modulated via the exchange coupling.

For simplification only pairs of two spin each are considered in the calculation.

With the Hamiltonian for the dipolar interaction

$$H = g^2 \mu_B^2 \left[ \frac{\hat{S}_1 \cdot \hat{S}_2}{r^3} - \frac{3 (\hat{S}_1 \cdot \hat{r}) (\hat{S}_2 \cdot \hat{r})}{r^5} \right]$$

(1)

with

$g = g$-factor

$\mu_B = \text{the Bohr magneton}$

$\hat{S}_i = \text{spin of electron } i$

$r = \text{the distance between the spins}$.

We obtain for the case of identical spins the following expression for the linewidth [18, 19]

$$\Delta B_{pp} = 6.56 \times 10^{-8} \frac{\mu_0^2}{(4 \pi)^2} \frac{\gamma^4 \hbar^2}{(2 \pi)^2} r^6 S(S + 1)$$

$$\left[ \frac{3}{8} (1 - 3 \cos^2 \Theta)^2 J(0) + \frac{9}{2} \sin^2 \Theta \cos^2 \Theta J(\omega) + \frac{9}{8} \sin^4 \Theta J(2 \omega) \right] [G]$$

with

$\gamma = \text{the gyromagnetic ratio}$

$J(\omega) = \text{the spectral density}$

$\Theta = \text{the angle between the vector connecting the spins and } B_0 \ (\Theta = 0 \text{ means collinear arrangement of } \hat{r} \text{ and } B_0)$.

The spectral density $J(\omega)$ is given by the spin diffusion. In the case of a quasi one-dimensional system, as assumed here, $J(\omega)$ follows an inverse square root dependence above a given cutoff frequency $\omega_c$, and is frequency independent below $\omega_c$ [20]:

$$\omega > \omega_c : J(\omega) \propto \omega^{-1/2}$$

$$\omega < \omega_c : J(\omega) = \text{constant}$$

$\omega_c$ is due to exchange perpendicular to the one-dimensional direction [21] and is introduced in most models to avoid the divergence of $\omega^{-1/2}$ when $\omega \to 0$. The existence of a cutoff frequency is proven by the fact that the lineshape is always Lorentzian [22, 23].

At 3.8 K a quantitative fit to the experimental data is achievable with a cutoff frequency of about 1.6 GHz, which is by a factor 6 lower than the measuring frequency. We are, therefore, close to the slow exchange limit [24]. The calculated curve is given in figure 6 as a solid line. At 100 and 296 K, qualitatively, this model still holds, but concomitantly with the much higher spin concentration which is present at these temperatures, there are additional contributions from spin pairs constituted of spins on different stacks. These pairs have to be taken into account. The contribution from these pairs is orthogonal to that introduced above. The resulting linewidth is therefore

$$\Delta B_{pp}^{\text{mot}}(\Theta) = \Delta B_{pp}(\Theta) + q \Delta B_{pp}(\Theta + 90^\circ).$$

(3)
A fraction of $q = 25\%$ holds for the 100 K as well as for the 296 K results. Not too surprising if one takes into account that the susceptibility (Fig. 4) does not change very much in this temperature range.

Whether this fraction $q$ is due to concentration effects or due to different distances within the two orthogonal pairs can not be distinguished as long as the proper crystal structure is unknown.

The fact that we always have one Lorentzian shaped ESR line, and not a superposition of the individual contributions from the different pairs, clearly shows that there is some exchange perpendicular to the one-dimensional direction. The cutoff frequency of about 0.2-1 GHz as deduced from the fits of our curves is fast enough to realize the averaging of the different contributions within the time scale of our experiment.

In conclusion; The low conductivity of $(bEDODBF)_2(AsF_6)_2(CH_2Cl)_0.2$, is due to thermal activation of electrons from defect states in the band gap to an empty conduction band. The band gap is rather large $> 0.4$ eV. The gap is opened by the perturbative potential from the anions which has a periodicity equal to $2k_F$ in the case of strong electron-electron repulsion. The strong electron-electron repulsion gives rise to a high susceptibility, and the electrons are localized and ordered in an antiferromagnetic way. The angular dependence of the ESR linewidth corresponds to dipole-dipole interaction in the intermediate exchange limit with one-dimensional spin diffusion. The ESR data also gives evidence for a structural phase transition at 150 K.

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References

[6] $^1H$ NMR (200 MHz): 7.24 (s 2H), 7.00 (s 2H), 4.30 (s 8H). MS (70 eV): 284 (M$^+$ 100 %), 228 (66 %), 200 (11 %), all other peaks below 10 %.