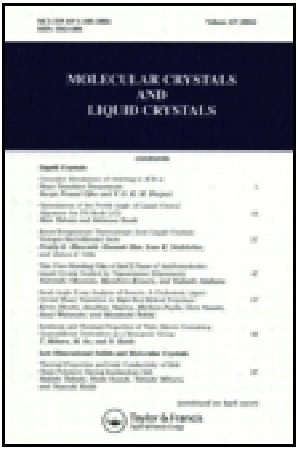

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2,3;7,8-Bis(ethylenedioxy)thianthrene-hexafluoroarsenate [(bEDOT)AsF_6]: A Mott-Hubbard Insulator Showing Evidence for Appreciable Correlation Effects

S. Söderholm [a], J. Noreland [b], G. Olovsson [b], I. Olovsson [b], J. Hellberg [c] & L. Engman [c]

[a] Department of Materials Science, The Royal Institute of Technology, S-100, 44, Stockholm, Sweden

[b] Institute of Chemistry, University of Uppsala, Box 531, S-751, 21, Uppsala, Sweden

[c] Department of Organic Chemistry, The Royal Institute of Technology, S-100, 44, Stockholm, Sweden

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2,3;7,8-Bis(ethylenedioxy)thianthrene-hexafluoroarsenate [(bEDOT)AsF_6]: A Mott-Hubbard Insulator Showing Evidence for Appreciable Correlation Effects

S. SÖDERHOLM

Department of Materials Science, The Royal Institute of Technology, S-100 44 Stockholm, Sweden

J. NORELAND, G. OLOVSSON and I. OLOVSSON

Institute of Chemistry, University of Uppsala, Box 531, S-751 21 Uppsala, Sweden

and

J. HELLBERG and L. ENGMAN

Department of Organic Chemistry, The Royal Institute of Technology, S-100 44 Stockholm, Sweden

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The structure, electrical, optical and magnetic properties of the title compound are reported. The stacks of anions and cations are segregated. The cation stack is dimerized and the bEDOT molecules are tilted; the angle relative to the stacking axis is 48°. (bEDOT)AsF_6 is semiconducting with $\sigma(300\ K) = 2 \cdot 10^{-8}\ (\Omega cm)^{-1}$ and the energy gap is about 1 eV. The optical absorption measurements give evidence for appreciable correlation effects. The on-site and the nearest-neighbor Coulomb repulsions are estimated to 1.5 and 0.6 eV, respectively, and the effective transfer integral to 0.2 eV. The observed ESR signal originates from defects/impurities present in a concentration of $4 \cdot 10^{18}$ spins/mole.

1. INTRODUCTION

In our study of electrical and magnetic properties of new organic conductors, the work has so far been concentrated on cation radical salts prepared from alkoxylated aromatic donors.[1-3] In order to extend the research on this class of quasi one-dimensional organic conductors we have recently synthesized several new donors of dibenzo-1,4-dichalcogenines.[4] One reason for extending the studies from alkoxylated dibenzofuranes to this class of donors is to obtain more information about the interplay between the donor structure and the physical properties of the cation radical salt. In the dibenzo-1,4-dichalcogenines one or two of the heteroatoms is sulphur, selenium, or tellurium (instead of a single oxygen in the previously studied systems.[1-3] The introduction of a higher chalcogen in the aromatic core might increase the transfer integral between the molecules in the stack of donors, via the increasing size of the π-orbital of the heteroatom along the stack. The charge and spin distribution will thus be changed which could strongly affect the properties of the cation radical salt. Furthermore, similar donor systems form mixed stack charge-transfer complexes with TCNQ,[5-11] and segregated stack CT-complexes with iodine.[9,10,12] A few electrochemically prepared cation radical salts are also known.[9,10,13,14] The so far quite meagre reporting and discussion on the physical properties of the cation radical salts and the influence on physical properties via the crystal structure, which is very sensitive to alterations of the donor molecule, motivated us to investigate 2,3;7,8-bis(ethylenedioxy)thianthrene-hexafluoroarsenate, [(bEDOT)AsF_6]. Its structure, electrical, optical and magnetic properties are reported in this communication. For experimental details see Refs. 2 and 3.

2. RESULTS

Crystal Structure

Single crystal X-ray diffraction experiments with MoKα-radiation gave a monoclinic structure, C2/*m* or C2, where the choice of space group depends on how the disorder found in the structure is treated. The cell parameters are at 295 K: a = 18.029(3) Å, b = 10.630(2) Å, c = 9.389(2) Å, β = 94.12(2)°, V = 1795(1) $Å^3$ and Z = 4. A refinement in space group C2/*m* of 185 independent parameters using 2252 unique reflections (with $\sin\theta/\lambda \leq 0.827$ $Å^{-1}$) gave an agreement factor $R(F^2)$ = 6.8% and $\sigma(C - C) = 0.007$ Å for bonds between non-disordered carbon atoms.

The asymmetric unit in space group C2/*m* consists of half a $bEDOT^+$ and half an AsF_6^- ion, where the arsenic atom is in a special position (in a mirror plane). All other atoms are in general positions. All the fluorine atoms in the AsF_6^- ion are disordered and have been refined to two different positions each. The ethylene groups at both ends of the bEDOT molecule are also disordered. This is indicated by their unusually high temperature factors and the apparent carbon—carbon bond distance of 1.29(2) Å.

The positively charged bEDOT molecule is nonplanar with a dihedral angle of 11° between the normals to the least-squares planes of the two aromatic carbon rings in the molecule.

The bEDOT molecules are stacked along the *c*-axis. Each stack consists of dimers, which are tilted 48° relative to the *c*-axis (Figure 1). Six AsF_6^- ions surround each bEDOT dimer and each of these ions is part of a linear anion chain extending along the c-axis. The geometrical overlap within a dimer is almost perfect. The overlap between dimers is shown in Figure 2. (The detailed crystal structure will be published later by J. Noreland, G. Olovsson and I. Olovsson.)

Physical Properties

The room temperature conductivity of the title compound is low, $\sigma_{rt} = 2 \cdot 10^{-8}$ $(\Omega cm)^{-1}$, and the conductivity is activated with an activation energy $\Delta = 0.48 \pm$

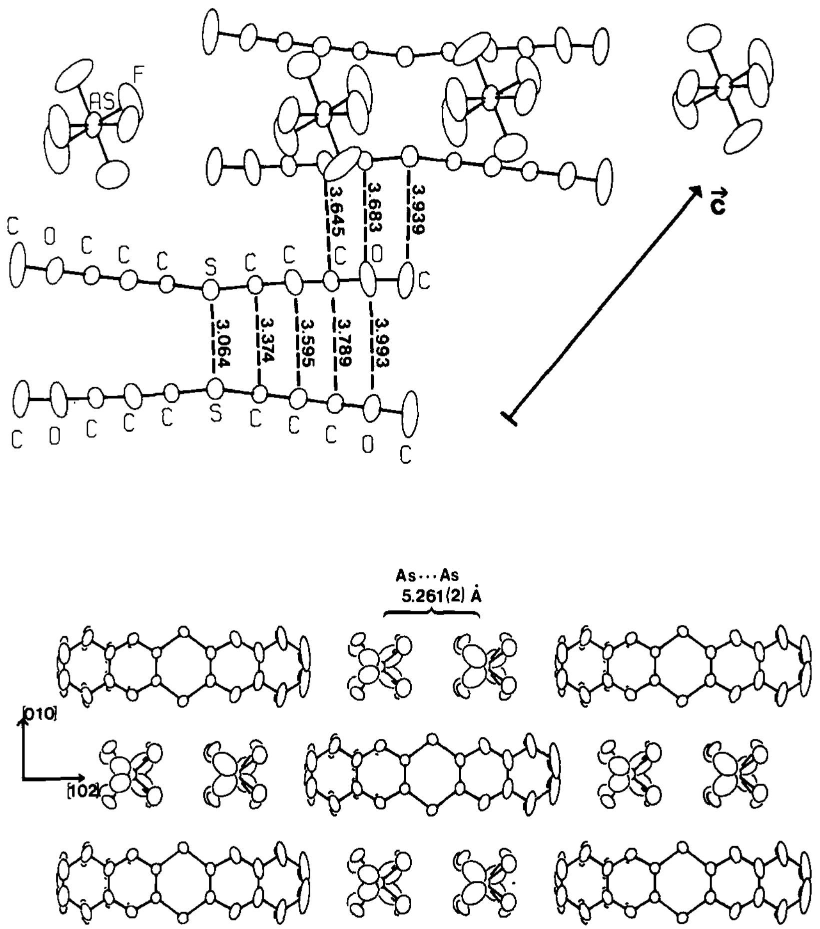

FIGURE 1 Top: The stack of bEDOT molecules in the *c*-direction, viewed in the *b*-direction (perpendicular to the mirror plane). The standard deviations are 0.002–0.006 Å. For clarity the AsF_6^- ions surrounding the lower dimer are omitted. Bottom: Arrangements around the bEDOT dimers viewed approximately perpendicularly to the mean molecular plane. The shortest S–F distance is 3.09(2) Å. Both orientations of the disordered AsF_6^- ion are shown in the figure.

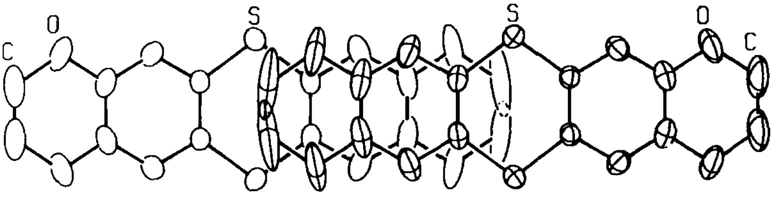

FIGURE 2 Molecular overlap between two adjacent dimers in a view perpendicular to the plane of the overlapping aromatic carbon rings.

0.02 eV in the investigated temperature range 300–250 K (Figure 3). The conductivity measurements were done with a standard four-probe technique. The high resistance of the crystals made measurements at lower temperatures impossible.

Optical absorption measurements were performed on composite samples, consisting of ground single crystals of (bEDOT)AsF$_6$ in a transparent and insulating matrix of KBr.

The spectrum of the donor bEDOT (Figure 4) is nearly constant with $\alpha \approx 800$ cm^{-1} in the investigated wavelength range 0.6–2.6 μm (2–0.5 eV). The spectrum of the cation radical salt shows a different behavior (Figure 4). Above 1.8 μm (0.69

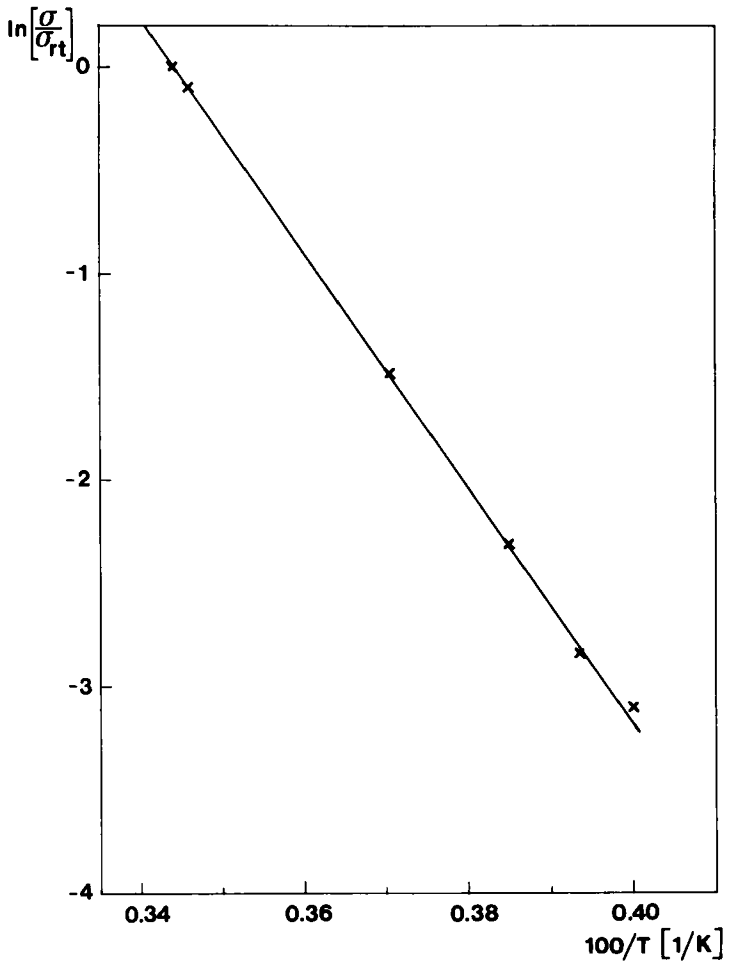

FIGURE 3 Normalized DC-conductivity of (bEDOT)AsF$_6$ vs. reciprocal temperature. $\sigma_{rt} = 2.80 \cdot 10^{-8}$ $(\Omega\text{cm})^{-1}$.

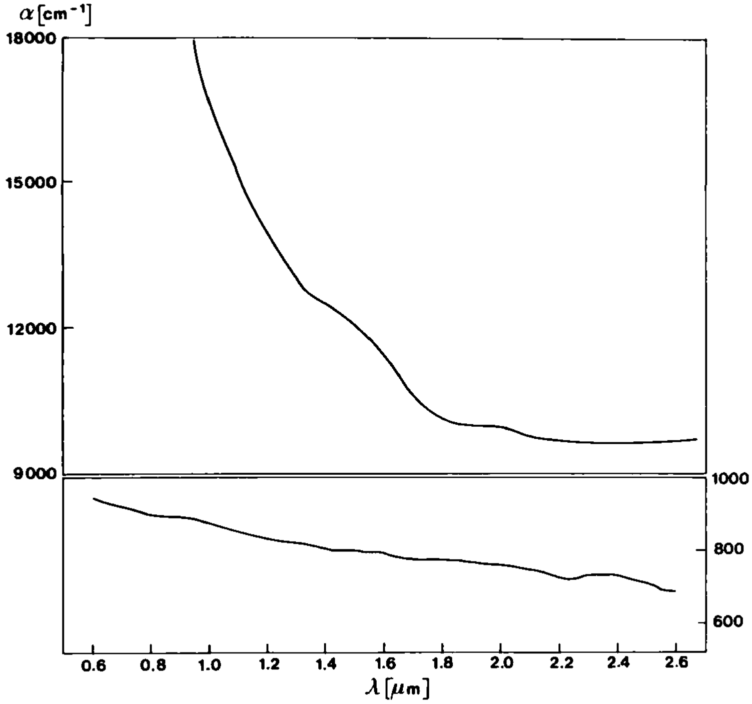

FIGURE 4 Lower panel: Absorption coefficient versus wavelength for bEDOT. Upper panel: Absorption coefficient versus wavelength for (bEDOT)AsF$_6$.

eV) the absorption is constant with $\alpha_{crs} = 9.6 \cdot 10^3$ cm^{-1}. At shorter wavelengths the absorption increases rapidly and α_{crs} is about $18 \cdot 10^3$ cm^{-1} at 0.9 μm (1.4 eV). It was not possible to measure the absorption at shorter wavelengths. Between 1.75 and 1.35 μm (0.71–0.92 eV) there is a shoulder on the otherwise smoothly increasing absorption coefficient curve.

By comparison of the signal intensity of the homogeneously broadened and Lorentzian shaped ESR signal with a calibrated sample the paramagnetic susceptibility was obtained, $\chi(300 \text{ K}) = 9 \cdot 10^{-9}$ emu/mole, *i.e.* $4 \cdot 10^{18}$ spins/mole. In Figure 5 the temperature dependence of the number of spins, *i.e.* the ESR intensity multiplied by T, is shown. The number of spins decreases with decreasing temperature down to 50 K. Below this temperature the number of spins is constant, *i.e.* a Curie law behavior is observed. The number of spins in the Curie tail is 6%.

The ESR linewidth ΔB_{pp} increases slowly from 1 G at 300 K to 2 G at 50 K; at lower temperatures the linewidth increases faster to reach a value of 4 G at the lowest investigated temperature 3.8 K (Figure 5).

The g-factor is rather high (2.0086) and constant above 50 K. When the temperature is decreased below 50 K the g-factor decreases slowly and $g = 2.0084$ at 3.8 K (Figure 5).

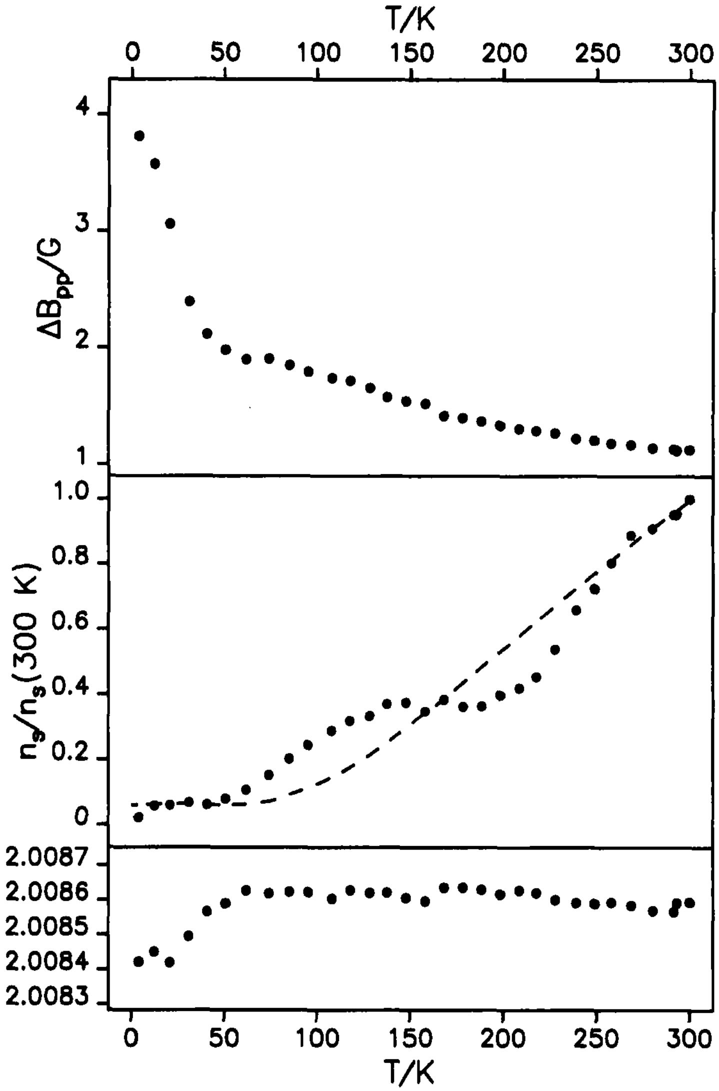

FIGURE 5 The temperature dependence of the linewidth, the number of spins, *i.e.* the ESR intensity multiplied by T (the dashed curve is calculated with an activation energy of 400 K (35 meV) for the number of spins and a Curie tail of 6%), and the g-factor. Orientation of the crystal: narrowest linewidth.

3. DISCUSSION

The physical properties of (bEDOT)AsF_6 will be interpreted in terms of the Hubbard model,[15,16] since the charge-transfer $\rho = 1$. In this case every donor is ionized, and in order to move an electron along the stack the repulsive energy between two electrons on the same bEDOT molecule has to be overcome. Thus, the material is a semiconductor. The dimerization of the bEDOT stack is taken care of by assuming that $t_1 > t_2$, where t_1 is the transfer integral within a dimer and t_2 is the transfer integral between adjacent dimers. This assumption is justified by the large difference in the geometrical overlap within a bEDOT dimer and between adjacent dimers. In this case the stack of bEDOT molecules can be treated as a regular stack of closed shell units, *i.e.* dimers of bEDOT$^-$ ions. In this picture the Hubbard Hamiltonian can be reformulated into terms of electrons and holes.[17,18] From studies of this model and the original Hubbard Hamiltonian it is known that the magnitude of the effective repulsive energy[19] mainly depends on the electronic and geometric structure of the donor molecule and that the physical properties of the cation radical salt are also strongly affected by the shape of the donor stack, *i.e.* the transfer integral(s) along the stack of donors.[18,20] For a dimerized chain the energy gap for electrical conduction is[18] $\Delta E = [U^2 + 16t_1^2]^{1/2} - 2t_1 - 2t_2$, where U is the effective repulsive energy between two electrons on the same molecule, and t_1 and t_2 are the nearest-neighbor transfer integrals, *i.e.* the transfer integrals within a dimer and between adjacent dimers, respectively, and $t_1 > t_2$. This expression for ΔE is valid both for $U >> 4t_1$ and $U << 4t_1$.

In terms of electrons and holes the absorption spectrum of a semiconductor will have two major features; an absorption peak due to excitons superimposed on (or separated from) the absorption edge caused by excitations of electrons to extended states. The shoulder on the otherwise smoothly increasing absorpton curve in Figure 4 should therefore arise from the optical excitation of bound electron-hole pairs, and the onset of the band-to-band transition is found at about 0.9 eV. But the formation of bound electron-hole pairs demands the presence of electron–electron repulsion, *i.e.* $U > 0$. In order to get a better understanding of the importance of correlation effects in (bEDOT)AsF$_6$ the optical properties will be discussed in the limit $U >> 4t$, *i.e.* the Hubbard model, where solutions can be obtained. The shoulder on the absorption spectrum can be understood by a model proposed by Lyo.[21] This model is related to the one where this feature is the signature of the formation of bound electron–hole pairs, but Lyo's model takes correlation effects into account. Lyo has shown that the introduction of a nearest-neighbor Coulomb repulsion, V_1, in the case of $U >> 4t$ and $U - V_1 >> 4t$, a doubly occupied site and a hole can form a local state, *i.e.* a bound "electron"-hole state. This bound state "steals" intensity from the absorption band of the extended states. For an antiferromagnetically coupled ground state this bound state exists if $V_1 > 2t$. The bound state has an energy lower than the band gap, *i.e.* it is situated in the gap below the upper Hubbard band. In this model the shoulder on the absorption edge originates from optical transitions from the ground state to the bound state. From Figure 4 the width of this transition is found to be about 0.4 eV and the maximum of the partly hidden absorption peak is around 0.9 eV. The absorption peak of the bond state is resonant around $h\nu = U - V_1$ and the width is approximately $1/4V_1$. From this expression it is possible to estimate $V_1 \approx 0.6$ eV. This value is probably too low since processes that broaden the absorption peak are not taken into account. Using this value of V_1 the onsite repulsion is estimated to $U \approx 1.5$ eV. By introducing an effective transfer integral t_e[21,22] which takes into account the dimerization of the bEDOT chain it is possible to estimate the magnitude of the transfer integral of the salt. In a first order approximation t_e is given by the average of t_1 and t_2.[22] Using this value for t_e one obtains $t_e \approx 0.2$ eV from the expression for ΔE, here the magnitude of the onset of the interband absorption 0.9 eV (1.35 μm) has been used for ΔE. (Using the value of 0.96 eV from the conductivity data changes t_e to 0.17 eV.) From these values one sees that the condition $V_1 > 2t$ is fulfilled, and that (bEDOT)AsF$_6$ is a salt with intermediate correlations, *i.e.* $U \approx 4t$, which is the case of almost every simple 1:1 ion-radical salt.[18,23,24,25]

A slightly different model, also assuming that $U >> 4t$, has been proposed by Mazumdar and Soos.[16] They propose that the introduction of a sufficiently large nearest-neighbor repulsion V_1 would split the upper and the lower Hubbard bands into sub-bands. In this case the absorption peak appears around $U - V_1$ but an expression for the activation energy for charge transport is not given. However, from their results that $U \approx 3V_1$ and $V_1 \approx 3t$, one obtains $U \approx 1.5$ eV, $V_1 \approx 0.5$ eV and $t_e \approx 0.15$ eV. These values are in good agreement with the values obtained from Lyo's model. Thus, from the known physical properties of (bEDOT)AsF$_6$ it is not possible to distinguish between these models, *i.e.* whether the nearest-neighbor repulsion V_1 gives rise to a bound state in the band gap or splits the Hubbard bands.

It is clear, anyway, that correlation effects must be taken into account and are important in order to understand the optical properties of this salt and similar salts. It is probably sufficient to take only U and V_1 into account, since it has been shown[26] that more distant Coulomb interactions can be neglected.

If $U >> 4t_1$ the elementary spin excitations of a dimerized salt are triplet excitons, which have an activation energy less than the activation energy for electrical conduction.[18,23,27] The absence of triplet spin excitons in the ESR spectrum of (bEDOT)AsF$_6$ can be explained by a high activation energy of these excitations. With an activation energy of about the size of the activation energy for conduction, as found in many systems with thermally activated triplet excitons,[18,23,27,28] the concentration of triplet excitons can be calculated to be about 10^{-7}–10^{-9}, using an activation energy for these states of 0.4–0.5 eV. Although this can theoretically explain the low susceptibility observed it is somewhat difficult to understand the magnitude of the susceptibility, taking into account that the crystals used in the experiments are not perfect, *i.e.* they have stacking faults, etc. For an imperfect material a high susceptibility is expected even if the activation energy for triplet states is high since the stacks would consist of segments and every odd numbered segment would have an unpaired spin. The observed number of spins would in this case correspond to a separation of $\sim 1.4 \cdot 10^4$ Å between the defects/impurities which seems too large. However, the number of spins usually observed in clean insulating diamagnetic organic crystals is about the same, *i.e.* 10^{18} spins/mole.[29] This makes it difficult to rule out this explanation even if it gives a large separation between the paramagnetic centers.

Another way to explain the magnetic properties of (bEDOT)AsF$_6$ has been discussed mainly by Torrance and coworkers.[30,31] In many semiconducting organic materials the activation energy for electrical conduction Δ_σ is larger than the energy necessary to excite spins over an energy gap Δ_χ, without any formation of triplet states even if the stack is *n*-merized. It has been argued that this difference in activation energy between charge and spin is caused by the presence of significant correlation effects. This since, if the electrons were non-interacting $\Delta_\sigma = \Delta_\chi$, and in the limit of very strong interactions the localized and antiferromagnetically coupled electrons would give a thermally activated susceptibility arising from the excitation of triplet states. The ratio $\Delta_\sigma/\Delta_\chi$ is about 25 in the present case. This ratio is much larger than the one reported for other systems where this model is valid; in those cases $\Delta_\sigma/\Delta_\chi \approx 2-4$.[30,31] The large ratio found in (bEDOT)AsF$_6$ points to strong correlation effects and thereby to the presence of triplet excitons, which have not been observed. (See, discussion above.)

From the above discussion of the magnetic properties of (bEDOT)AsF$_6$ it is clear that correlation effects must be taken into account in order to explain the magnetic properties of this salt. From the considerations about the different models for the magnetic properties and the optical data we conclude that the former model for the spin properties, *i.e.* a Hubbard model, best describes these properties. This leads us to believe that the observed ESR signal arises from defects/impurities.

The number of spins (paramagnetic centers) decreases with decreasing temperature, except for a region between 200 and 150 K. This plateau is probably an artefact caused by the very weak ESR signal. We believe that we observe two different kinds of defect/impurity states; one state which is thermally activated with an activation energy of about 400 K (35 meV) above 50 K and another which gives rise to the Curie tail at lower temperatures (Figure 5). This interpretation is supported by the decrease of the *g*-factor around 50 K and the fact that the *g*-factor tends to another constant value below 25 K (Figure 5).

Measurements of the angular dependence of the linewidth and the *g*-factor showed that there was no correlation between the angular dependence of the *g*-factor and the linewidth as in the case of spin-orbit coupling. However, the high *g* value points to a contribution from spin-orbit coupling due to the sulphur. Furthermore the lack of any angular dependence of the linewidth which could be ascribed to dipole–dipole interactions makes us believe that the linewidth is mainly caused by unresolved hyperfine structure. The observed Lorentzian lineshape points to the presence of some exchange, which could explain the unresolved hyperfine structure.

In summary, the physical properties of (bEDOT)AsF$_6$ can be understood if correlation effects are taken into account. But there is still some doubt about the validity of the Hubbard model in the description of the electrical, optical and magnetic properties. This uncertainty is related to the fact that the correlation effects are of intermediate strength.

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