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Triplet excitons in the simple tetracyanoquinodimethane (TCNQ) salts $\mathrm{Rb}^{+}\mathrm{TCNQ}^{-}$ and $(\mathrm{trimethylbenzimidazolium})^{+}\mathrm{TCNQ}^{-}$

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The experimental dipolar splitting tensors of the triplet excitons and their contribution to the magnetic susceptibility are reported for two TCNQ (tetracyanoquinodimethane) salts, i.e., $\mathrm{Rb}^{+}\mathrm{TCNQ}^{-}$ and trimethylbenzimidazolium TCNQ^{-}. An exciton model intermediate between the localized and the free-electron limit is presented. Application of this model shows that the usual Heisenberg antiferromagnet treatment of these semiconducting TCNQ salts is not valid.

I. INTRODUCTION

Some years after the discovery of the ion-radical salts of TCNQ (tetracyanoquinodimethane), a large number of papers have been concerned with the thermally accessible triplet exciton states in the semiconducting salts, which are responsible for the paramagnetism in these compounds.[1,2] For the description of the phenomenon, commonly an effective exchange Hamiltonian of the Heisenberg-type is used;

$$\mathcal{H} = \sum_{i<j} J_{ij} \vec{S}_i \cdot \vec{S}_j . \tag{1}$$

To explain the sign and magnitude of the exchange integrals one has to allow for a contribution of ionic states in the singlet ground state.[3] An essential condition to justify such a description is that the electron repulsions, especially the repulsion between two electrons on the same molecule U, is much larger than the one-electron transfer integrals t_{ij}. Recent studies, however, show that it is doubtful that this condition is satisfied in TCNQ salts.[4,5] In a previous paper,[6] we have proposed an exciton model, which is not restricted to the limit where U is large. In Sec. II of this paper we will generalize this model and derive an energy-level scheme for simple TCNQ salts.

To verify these ideas we have studied the dipolar splittings and intensities of the triplet exciton lines discovered in two simple TCNQ salts, namely, $\mathrm{Rb}^{+}\mathrm{TCNQ}^{-}$ and $\mathrm{TMB}^{+}\mathrm{TCNQ}^{-}$, where TMB^{+} stands for the trimethylbenzimidazolium ion, which is diamagnetic. The preparation of the materials is described in Sec. III and the experimental results are presented in Sec. IV. Data on the temperature dependence of the line widths and splittings were published in a separate paper.[7] The arrangement of the TCNQ^{-} ions in $\mathrm{Rb}^{+}\mathrm{TCNQ}^{-}$ is typical for semiconducting TCNQ salts, i.e., the ions are stacked in alternating rows.[8] In $\mathrm{TMB}^{+}\mathrm{TCNQ}^{-}$ the ions are arranged in isolated pairs.[9] The crystal structures of the two compounds are depicted in Figs. 1 and 2, respectively. This difference in the crystal structure leads to remarkable differences in the dynamic behavior of the triplet excitons as was demonstrated before,[7] and might give rise to a different size of the exciton.[6]

II. SOME THEORETICAL CONSIDERATIONS

As we have pointed out in Sec. I, the electrons in TCNQ salts can neither be considered as free nor as localized. Both the tendency to delocalize and the electron repulsions, which oppose this tendency, are incorporated in a simple way in the

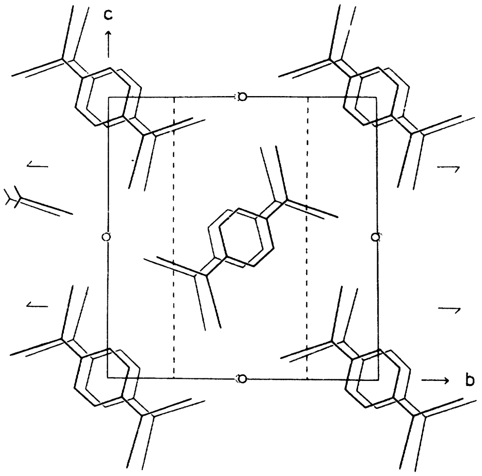

FIG. 1. In the crystal structure of $\mathrm{Rb}^{+}\mathrm{TCNQ}^{-}$ (Ref. 8), the TCNQ^{-} ions are stacked in rows. Two types of rows are present, connected to each other by (dashed) mirror-glide planes.

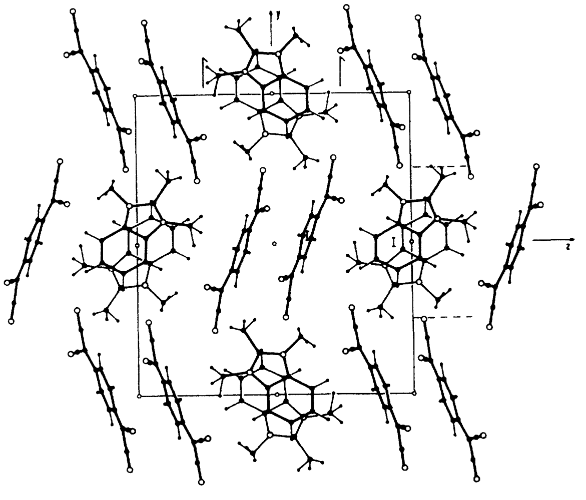

FIG. 2. In the crystal structure of TMB$^+$ TCNQ$^-$ (Ref. 9), the ions are arranged in pairs forming chains in the x direction. As in Rb$^+$ TCNQ$^-$ there are two types of rows connected by mirror-glide planes.

Hubbard Hamiltonian. For the alternating chain of ion radicals, this Hamiltonian may be written in the nearest-neighbor approximation as

$$\begin{aligned}\mathcal{H} = t_1 \sum_i \sum_\sigma \left(c^\dagger_{2i-1;\sigma} c_{2i,\sigma} + c^\dagger_{2i,\sigma} c_{2i-1,\sigma}\right) \\ + t_2 \sum_i \sum_\sigma \left(c^\dagger_{2i,\sigma} c_{2i+1,\sigma} + c^\dagger_{2i+1,\sigma} c_{2i,\sigma}\right) \\ + U \sum_i \sum_\sigma \left(n_{2i-1,\sigma} n_{2i-1,\bar\sigma} + n_{2i,\sigma} n_{2i,\bar\sigma}\right),\end{aligned} \tag{2}$$

The operators $c^\dagger_{2i,\sigma}$ and $c_{2i,\sigma}$ create or destroy an electron with spin σ in the valence state of a radical ion at site $2i$, and $n_{2i,\sigma} = c^\dagger_{2i,\sigma} c_{2i\sigma}$ is the corresponding number operator. t_1 and t_2 are nearest-neighbor transfer integrals, where we take t_1 to be larger than t_2. U is the effective[10] repulsive energy between two electrons on the same TCNQ molecule. Equation (2) is still too complicated to be solved. We will introduce the simplifying assumption that the alternation is strong or in other words that t_1 is much larger than t_2. In that case the system may be considered as a regular chain of closed-shell units, namely, dimers of TCNQ$^-$ ions. It is then possible to reformulate the problem in terms of electrons and holes.[11] The first one-particle excitations of the chain of dimers may be constructed from electron-hole pair states, for example states in which an electron has been excited from the ground state of one dimer to the excited state of another one, leaving a hole behind. Due to electron repulsions the electron and hole will attract each other and may form bound states. These are the exciton states, in which we are interested here. The Hamiltonian with respect to the ground state is now

$$\begin{aligned}\mathcal{H}_M = t^c \sum_i \left(a^\dagger_i a_{i+1} + a^\dagger_{i+1} a_i\right) - t^v \sum_i \left(b^\dagger_i b_{i+1} + b^\dagger_{i+1} b_i\right) \\ + \sum_i \sum_j \left(E_0 - I_M \delta_{ij}\right) a^\dagger_i a_i b^\dagger_j b_j .\end{aligned} \tag{3}$$

The operators $a^\dagger_i$ and $b^\dagger_i$ create an electron and a hole on a dimer at site i. t^c and t^v are nearest-neighbor transfer integrals between excited and valence states of a dimer respectively, E_0 is the energy of a free electron and a free hole, and I_M is the electron-hole attraction if the two particles are on the same dimer. M stands for singlet or triplet. This exciton problem, which is essentially a particular case of the exciton theory for a one-dimensional chain of closed shell entities of Merrifield,[12] was solved in our previous paper.[6]

The energy eigenvalues of the exciton states were found to be

$$E_M = E_0 - (I_M / |I_M|)[4\epsilon^2(K) + I_M^2]^{1/2} , \tag{4}$$

with

$$\epsilon(K) = [(t^c)^2 + (t^v)^2 - 2t^c t^v \cos(Ka)]^{1/2} .$$

K is the wave vector of the exciton and a is the distance between two dimers. The exciton wave-function decreases exponentially as a function of the electron hole distance. It is worth noting that if N is the number of dimers in a chain, there are N-singlet and N-triplet exciton states. Because we started with $4N^2$ electron hole pair states, including spin, the remaining $4N(N-1)$ states form a band of uncorrelated electron-hole pair states with energy[12]

$$E_u = E_0 - 2\epsilon(K) \cos(\lambda a) , \tag{5}$$

where λ is a quantum number having $N-1$ values between the values of the series π/Na, $2\pi/Na$, $3\pi/Na, \ldots, \pi/a$. These states correspond to the perturbed free-electron and hole states of the valence and conduction bands. The resulting energy-level diagram is given in Fig. 3. The above model contains the essential features to explain the most important properties of simple TCNQ salts, namely the electrical conduction and the magnetism.

We will now relate the quantities t^v, t^c, E_0, and I_M of the electron-hole description to the more useful quantities t_1, t_2, and U in the Hubbard Hamiltonian equation (2).

It is easily seen that both the quantity t^c and $-t^v$, the energy required to transfer an electron and a hole, respectively, from one dimer to its neighbor are equal to $\frac{1}{2}t_2$. In order to calculate the

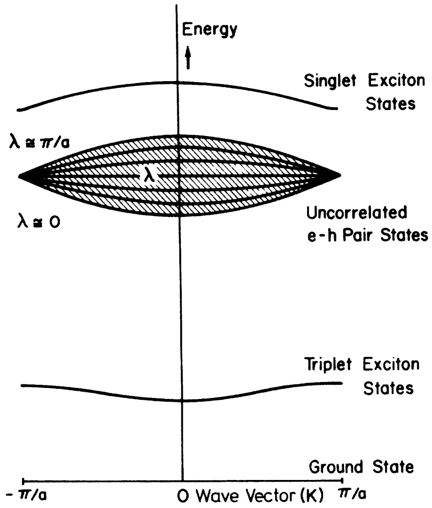

FIG. 3. Energy-level diagram for an alternating chain consisting of N radical ions. Because of on-site electron-hole interaction a band of N triplet and a band of N singlet bound states separate from the main band of electron-hole pair states, leaving $N-1$ bands of N free-electron–hole pair states. The triplet exciton states are mainly responsible for the magnetism of the system, whereas the free electrons and holes in the band of uncorrelated electron-hole pair band of states are responsible for the semiconducting properties.

quantities E_0 and I_M, it was assumed in (6) that t_1, the intradimer transfer integral is much larger than the Hubbard U. This condition is unnecessarily restrictive and will be removed in what follows. The on-site electron-hole attraction I_M is the difference between the energy of a free-electron-hole pair (E_0), and the energy of a dimer in the excited triplet or singlet state. Recently, Suezaki has calculated the energy levels of a radical dimer in the Hubbard approximation.[13] The energies of the three singlet states S_0, S_1, and S_2 are $\frac{1}{2}U-R$, U, and $\frac{1}{2}U+R$, respectively, and the energy of the triplet state is zero (see also Fig. 4). Here R is given by

$$R=[(\tfrac{1}{2}U)^2+(2t_1)^2]^{1/2}. \qquad (6)$$

Thus, the energies of the first-excited singlet and triplet states of an isolated dimer with respect to the ground state are

$$E_T^0=R-\tfrac{1}{2}U \quad \text{and} \quad E_S^0=R+\tfrac{1}{2}U. \qquad (7)$$

The quantity E_0 is the energy of an electron on one dimer and a hole on another one, the pair of dimers being noninteracting. We will use Hamiltonian (2) with $t_2=0$ and $i=1,2$. The states, forming a basis for the eigenvalue problem, are of the type

$$c_{1\alpha}^\dagger c_{3\alpha}^\dagger c_{3\beta}^\dagger c_{4\beta}^\dagger |0\rangle\,, \qquad (8)$$

where $|0\rangle$ is the vacuum state. There are 32 states of this kind giving rise to eight singlet and eight triplet states. The solution of the eigenvalue problem is straightforward. Two singlet and two triplet states have the energy $U-2t_1$, four singlet and four triplet states have energy U, and two singlet and two triplet states have the energy $U+2t_1$. We are interested in the energy of the lowest free-electron-hole pair states with respect to the ground state. The energy of the ground state is obviously two times the ground state energy of the single dimer problem discussed above, i.e., $U-2R$. Consequently,

$$E_0=2R-2t_1\,; \qquad (9)$$

and combining Eqs. (6) and (8),

$$I_T=E_0-E_T^0=R-2t_1+\tfrac{1}{2}U\,, \qquad (10a)$$

$$I_S=E_0-E_S^0=R-2t_1-\tfrac{1}{2}U\,. \qquad (10b)$$

Equations (9) and (10) should be used together with Eqs. (4) and (5). In Fig. 4 schematically the quantities calculated above are depicted for the single dimer, two isolated dimers, and a chain of weakly interacting dimers.

In the above model, electron-phonon interactions have not been considered. Evidence that these interactions effect the dynamics of the triplet excitons in TCNQ salts was presented in another paper.[7] The motion of the excitons is not coherent as would be expected on the basis of the above model, but diffusive. The excitons are self-trap-

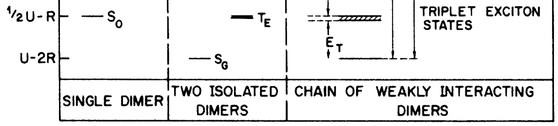

FIG. 4. Energy-level scheme in the Hubbard approximation for a single dimer, two isolated dimers, and a chain of weakly interacting dimers. In addition to the levels corresponding to the single dimer problem a pair of degenerate singlet and triplet levels appear in the case of the double dimer, which are charge-transfer states. If one allows for weak-transfer interactions between the dimers in a chain, the states of the isolated-dimer problem broaden into bands.

TABLE I. Summary of the results of Sec. II.

Quantity	General	Localized electron limit $4_{t1}/U \ll 1$ $t_2 < t_1$	Dimer limit $4t_1/U \gg 1$ $t_2 < t_1$
Triplet excitation energy	$E_T = 2R - 2t_1 - (4t_2^2 + I_T^2)^{1/2} - E_L$	$\frac{4t_1^2}{U} - \frac{4t_2^2}{U} - E_L$	$2t_1 - [4t_2^2 + (\frac{1}{2}U)^2]^{1/2} - E_L$
Energy gap for electrical conduction	$E_g = 2R - 2t_1 - 2t_2$	$\frac{1}{2}U$	$2t_1 - 2t_2$
Binding energy for triplet exciton	$I_T = R - 2t_1 + \frac{1}{2}U$	U	$\frac{1}{2}U$
Energy of formation for a free *e-h* pair	$E_0 = 2R - 2t_1$ $R = [4t_1^2 + (\frac{1}{2}U)^2]^{1/2}$	U	$2t_1$

ped, i.e., the triplet excitation is accompanied by a local lattice distortion. The reason is that there is no binding in the excited triplet state in contrast to the ground singlet state of a single dimer. Consequently, the ions of a dimer excited to the triplet state move apart, resulting in a slight lowering of the energy. This self-trapping energy E_L has to be subtracted from the triplet excitation energy of Eq. (3), where K has been set to zero, i.e.,

$$E_T = E_0 - (4t_2^2 + I_T^2)^{1/2} - E_L\,. \qquad (11)$$

The above results have been summarized in Table I. Note that in the extreme limit, where t_1 is small with respect to U, one gets the results for a strongly alternating antiferromagnetic chain with $J_1 = 4t_1^2/U$. In the opposite limit, the results are those for the tight binding one electron approach.[4] The excitons then are of the Wannier type.

Finally, we argued in Ref. 6 that the dipolar splitting parameters are expected to be smaller than the calculated values for an isolated dimer in the triplet state, because the exciton spreads over more than one molecule, if the $2t_2/U$ ratio is not very small. As was shown there, the relative magnitude of the dipolar splittings is given by

$$\Lambda_{ml}/\Lambda_{ml}^0 \approx (1 + 4t_2^2/I_T^2)^{-1/2}\,, \qquad (12)$$

where m,l denote the principal axes, Λ_{ml} stands for any experimental dipolar splitting tensor element, and Λ_{ml}^0 is the corresponding one for an isolated dimer. Also, here we have set K to zero because the exciton is localized by a lattice polarization.

III. EXPERIMENTAL

TCNQ was synthesized following the procedure outlined by Acker and Hertler.[14] The raw material was recrystallized from acetonitrile and sublimed *in vacuo*. The Rubidium salt was prepared by mixing solutions of the iodide and of TCNQ in acetonitrile.[15] Although small crystals of these salts could be obtained by slowly cooling a saturated solution of these materials, much larger crystals were grown by the diffusion technique described by Pott and Kommandeur.[16] In the case of $\mathrm{Rb^+TCNQ^-}$ two distinct phases are usually obtained.[17] The phase we studied was Vegter's RbTCNQ I, the reddish-purple needles, the crystal structure of which has been determined by Hoekstra *et al.*[8]

The only way to prepare $\mathrm{TMB^+TCNQ^-}$ is from a 1, 2, 3-trimethylbenzimidazolium salt and $\mathrm{Li^+TCNQ^-}$. $\mathrm{TMB^+}$ iodide was synthesized starting from 2-methylbenzimidazole. Methylation of the compound was accomplished in two steps. *N*-methyl-2-methylbenzimidazole was prepared by slowly adding 15 g of methyliodide to a solution of 13 g of 2-methylbenzimidazole and 6 g of potassium hydroxide in 10 ml of methanol. After the vigorous reaction was completed, the white solid was collected, washed with several small amounts of water and dried in air (melting point 58 °C), 12 g of this material were dissolved in 10 ml of methanol. An equimolar amount of methyliodide was added and the mixture was allowed to stand overnight. The white solid was collected, washed with methanol and recrystallized two or three times from methanol or ethanol. Seven grams of white plates (melting point 247 °C) were left. Elemental analysis gave the following results: C :41.48 (41.68); H :4.60 (4.54); N :9.58 (9.72); I:44.23 (44.08).

Quite-large single crystals of $\mathrm{TMB^+TCNQ^-}$ ($5 \times 5 \times 1$ mm) were obtained by slow cooling (0.005 °C/min) of a saturated solution of the compound in acetonitrile, in which a small-seed crystal was suspended.

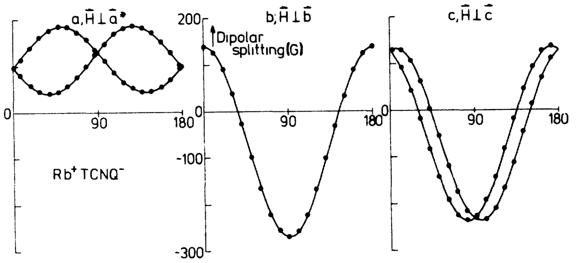

FIG. 5. Dipolar splittings (in gauss) for rotations with the magnetic field perpendicular to the a^*, b and c axes of a Rb^+ $TCNQ^-$ crystal. The two curves are due to the two magnetically equivalent kinds of excitons originating from the two symmetry-connected types of rows of $TCNQ^-$ ions (see Fig. 1).

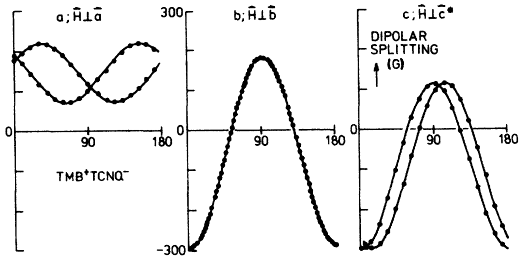

FIG. 6. Dipolar splittings (in gauss) for rotations with the magnetic field perpendicular to the a, b and c^* axes of a TMB^+ $TCNQ^-$ crystal. The two curves are due to the two magnetically inequivalent kinds of excitons, originating from the two symmetry connected types of $TCNQ^-$ dimers (see Fig. 2). The weak additional fine structure present in this material has been left out of the figure.

The ESR measurements were performed with Varian E3 and E9 ESR spectrometers.

IV. RESULTS

A. Dipolar splittings

In Rb^+TCNQ^- a first-order phase transition occurs at 376 °K, as is evidenced by temperature-dependent x-ray diffraction and heat of transition data.[18] At this temperature, the overall magnetic susceptibility shows a substantial increase. We have observed triplet exciton lines in the ESR spectra of the low-temperature phase. In Fig. 5, the dipolar splittings are presented as a function of the angle of rotation of the crystal with respect to the magnetic field, around three mutually perpendicular axes, i.e., the a^*, b, and c axes at -10 °C. For an arbitrary direction of the magnetic field, two pairs of lines are observed, originating from the two translationally inequivalent rows of $TCNQ^-$ ions, which are connected to each other by a mirror plane perpendicular to the b axis (see Fig. 1). In Table II, the dipolar splitting tensor elements in the a^*bc axes system, and the dipolar splitting parameters D and E have been collected, together with the corresponding calculated quantities for a pair of $TCNQ^-$ ions with the shortest interplanar distance in the actual crystal structure of Rb^+TCNQ^-, and the ratio between the experimental and calculated quantities. For the calculation we refer to Ref. 19.

In Fig. 6, the orientational dependence of the dipolar splittings are drawn for rotations of a TMB^+TCNQ^- crystal around the a, b and c^* axis. Just as in the case of Rb^+TCNQ^- generally two pairs of regular exciton lines are observed, which coincide, if the magnetic field is parallel or perpendicular to the b axis. The tensor elements deduced from this figure for the regular excitons and the D and E values are given in Table II. Again the corresponding quantities for an isolated dimer in the crystal structure of TMB^+TCNQ^- and the ratio between the experimental and calculated

TABLE II. Dipolar-splitting tensor elements and dipolar-splitting parameters D and E (in MHz) for Rb^+TCNQ^- and TMB^+TCNQ^-.

Compound	x, y, and z refer to	Λ_{xx}	Λ_{yy}	Λ_{zz}	Λ_{xy}	Λ_{yz}	Λ_{xz}	D	E
Rb^+TCNQ^-	a^*, b, c								
exper. (264 °K)		−214	123	91	−42	±64	±112	392	47.6
calc.		−323	179	144	−103	±110	±171	617	69.7
ratio		0.66	0.69	0.63	0.41	0.58	0.65	0.64	0.68
TMB^+TCNQ^-	a, b, c^*								
expt. (293 °K)		169	100	−269	±60	±47.5	−45	421	63.5
calc.		222	154	−376	±61	±55	−36	577	65.5
ratio		0.76	0.69	0.72	0.98	0.86	1.25	0.73	0.97

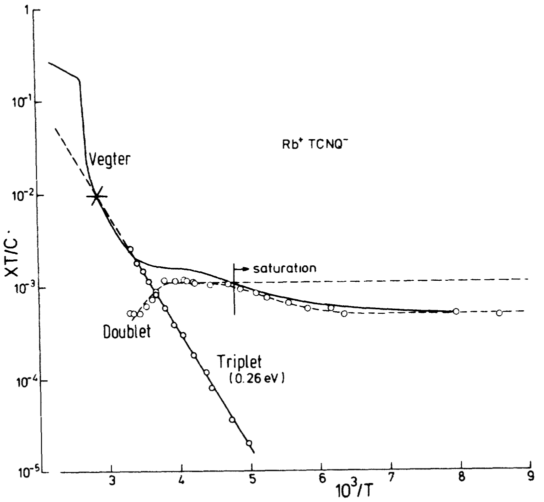

FIG. 7. Total magnetic susceptibility of $\mathrm{Rb^+\,TCNQ^-}$ as determined by Vegter (Ref. 17) and the separate contributions due to triplet and doublet species in units of $\chi T/C$ (fraction of spin-$\frac{1}{2}$ species). χ is the molar magnetic susceptibility, T is the temperature, and C is the Curie constant.

quantities have been added.

In $\mathrm{TMB^+TCNQ^-}$, not only the regular exciton lines were observed, but in addition, a rather complex fine structure. The intensity of these additional lines is some orders of magnitude smaller than that of the regular triplet exciton lines. The structure was present in all crystals of $\mathrm{TMB^+TCNQ^-}$ we studied, both in crystals, grown from acetonitrile or methanol. This additional structure is probably due to higher excited magnetic exciton states like electron transfer and excitonic molecule states.[20]

B. Intensities

The relative intensities of the ESR signals were obtained by calculating the product of the height and the square of the width of the derivative of the absorption line. This procedure is justified if the lines have a Gaussian or a Lorentzian line shape. The line shape of the triplet lines is very near to a Lorentzian in all cases. The line shape of the doublet signal deviates only slightly from a Lorentzian. Absolute intensities were obtained by fitting our results to the high-temperature overall magnetic susceptibility data of Vegeter[17] for $\mathrm{Rb^+TCNQ^-}$ and those of Dupuis *et al.*[21] for $\mathrm{TMB^+TCNQ^-}$. This was done by an extrapolation of our data on the triplet exciton lines to a temperature at which the intensity of the doublet signal is negligible and assuming, that this value is equal to the value given by Vegter and by Dupuis *et al.* Our results are depicted in the Figs. 7 and 8, together with the data of Refs. 17 and 21. The points at which our results have been fitted to theirs have been marked by crosses.

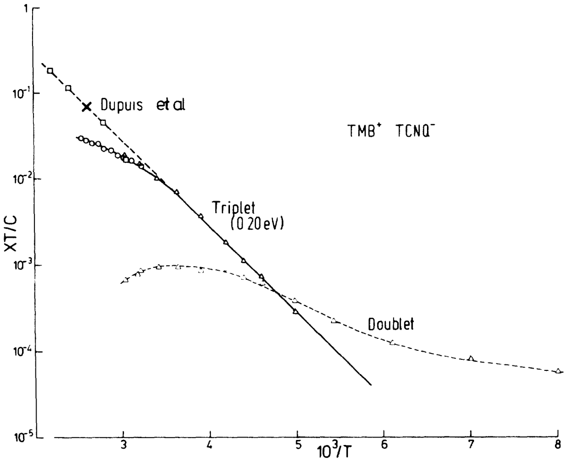

FIG. 8. Total magnetic susceptibility of $\mathrm{TMB^+TCNQ^-}$ as determined by Dupuis (Ref. 21) and the separate contributions due to triplet and doublet species in units of $\chi T/C$.

The doublet line generally consists of a narrow and a broad line.[2] In both $\mathrm{Rb^+TCNQ^-}$ and $\mathrm{TMB^+TCNQ^-}$ the intensity of the narrow line changes irreproducibly during a temperature cycle and the data have been omitted from Figs. 7 and 8. The relative intensity of the broad doublet line with respect to the intensity of the triplet exciton lines varied strongly from crystal to crystal. (Differences of a factor of 10 were not exceptional.) Furthermore, the intensity is approximately proportional to T^{-1} suggesting that the species which are responsible for the central signal are either magnetic impurities or excess electrons or holes. The intensities of the triplet exciton lines are given by

$$\chi_M T/C = A \exp(-E_T/kT)\,, \tag{13}$$

where C is the Curie constant.

The values for E_T and A deduced from Figs. 7 and 8 are collected in Table III. The values obtained from the intensity measurements of the

TABLE III. Pre-exponential factors and activation energies for the triplet exciton contribution to $\chi T/C$.

Compound	A	$E_T(\Delta m=1)$[a]	$E_T(\Delta m=2)$[b]	$E_T(\chi_{\text{total}})$
$\mathrm{Rb^+TCNQ^-}$	~40	0.26	0.29	0.35[c]
$\mathrm{TMB^+TCNQ^-}$	~30	0.20	0.17	0.20[d]

[a] This work.
[b] Reference 19.
[c] Reference 17.
[d] Reference 21.

$\Delta m = 2$ signals[19] and the values which may be derived from the data of Refs. 17 and 21 have been added for comparison. The values obtained for $\Delta m = 1$ lines of a single-crystal spectrum are certainly the most accurate ones. The pre-exponential A is much larger than one in both cases indicating, that the excitation energy depends on temperature: $E = E_0 - cT$. A change in the intermolecular distances with temperature could be responsible for this.

V. DISCUSSION

In this section, we will try to evaluate the parameters of the model of Sec. II for the two simple TCNQ salts studied from experimental quantities, i.e., (i) the triplet excitation energy, which is given by Eq. (11); (ii) the activation energy for conduction, which should be equal to half the energy gap between the valence and conduction band or $E_g = E_0 - 2t_2$; (iii) the dipolar splitting tensor elements, which should satisfy Eq. (12).

For Rb^+TCNQ^-, Vegter has calculated the transfer integrals t_1 and t_2 in the actual undistorted structure to be 0.16 and 0.046 eV, respectively.[17] Although these values give only the order of magnitude of these quantities, the ratio of 3.5 probably is quite reliable. This value is large enough to justify the application of the model of Sec. II. The conductivity of single crystals of the reddish-purple phase of Rb^+TCNQ^- was measured by Sakai *et al.*[22] They found an activation energy for conduction of 0.44–0.53 eV. Consequently, we have $E_g \simeq 1$ eV. From Table III, the triplet excitation energy is 0.26 eV and the self-trapping energy E_L was determined experimentally as 0.08 eV.[7] Using Eq. (11), we get $E_T + E_L = 0.34$ eV. From Eqs. (6)–(12), and using the t_1/t_2 ratio of 3.5, U and t_1 can be estimated. The result is $U = 1.3$, $t_1 = 0.4$ eV.

The model should be ideally applicable to TMB^+TCNQ^- because the dimers are well isolated from each other in this material and we can neglect the one-electron band width. The conductivity was measured by Dupuis.[23] The activation energy he gives is 0.56 eV. The triplet excitation energy was 0.20 eV (Table III) and the self-trapping energy $E_L = 0.15$ eV.[7] In a similar way as in the case of Rb^+TCNQ^- taking t_2 equal to zero, we get $U = 1.1$ eV, $t_1 = 0.35$ eV. These values are comparable to the values obtained for Rb^+TCNQ^-.

The ratio of the experimental dipolar splitting tensor elements and the calculated ones for an isolated dimer are for both Rb^+TCNQ^- and TMB^+TCNQ^- smaller than one, as is evident from Table II. There appear to be two reasons for this reduction. In the first place, there is the delocalization of the exciton due to the transfer integral t_2.[6] In RbTCNQ a fraction t_2/U of the exciton would be on the neighbors, yielding a ratio of 0.9, which is still too large. Also, in TMB^+TCNQ, almost no delocalization would occur, since t_2 is so small. Recently, Silverstein and Soos[25] suggested that the triplet would be localized not on the two most-closely-spaced ions, but on the ions most widely separated, since that appeared to give better agreement with the calculated values of the dipolar tensor. Apart from the fact that one can then not understand, why the substance should dimerize at all and spend lattice energy on pushing two ions together, clearly in TMB^+TCNQ such an interpretation is impossible because of the different structure of the chain. A better explanation is given by the introduction of what one could call "Peierls pairs." The chain dimerizes because it can be shown, both for $4t \ll U$ and for $4t \gg U$, and therefore also for $4t \approx U$ that an alternating chain has the lowest energy. This Peierls or spin-Peierls effect also leads to the Peierls transition at higher temperatures, which occurs generally in these compounds.[17] Locally, upon excitation of the triplet, the binding energy of the two ions involved is reduced to zero, and the ions move away from one another. We therefore observed an activation energy (0.08 eV for RbTCNQ and 0.16 eV for TMB^+TCNQ) for the exciton motion.[7] Obviously, we see the ESR of the ions at their "new" sites, where their distance is greater. The further reduction of D, which is most sensitive to this effect is of the order of 25% in both Rb^+ and TMB^+TCNQ, requiring a change in $\langle r \rangle$ of about 10% or 0.32 Å, which is very close to the crystallographically measured alternation of $3.484 - 3.159 = 0.325$ Å. "Peierls pairs," i.e., locally dedimerized lattice sites therefore appear to give a satisfactory explanation for the reduction of D.

In K^+TCNQ^- the dipolar splitting is so small that the triplet must be delocalized over more than one dimer,[24] which is probably connected to the smaller ratio of t_1/t_2 which one would estimate for this structure.[26]

VI. CONCLUSIONS

As was pointed out in Sec. II, the situation described by Hamiltonian (1) may be derived from our results in the limit where $2t_1$ is much smaller than U. For both Rb^+TCNQ^- and TMB^+TCNQ^- we arrive at a $2t_1/U$ ratio of about 0.6. This value obviously does not justify the system to be treated as a linear Heisenberg antiferromagnet. On the other hand, also a simple band theoretical treatment as was applied by Vegter *et al.*[17] to the simple alkali TCNQ salts is not allowed. This result shows that these materials should be considered as strongly correlated narrow-band systems.

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[1] The subject was reviewed by P. L. Nordio, Z. G. Soos, and H. M. McConnell, Ann. Rev. Phys. Chem. 17, 237 (1966).

[2] J. C. Bailey and D. B. Chesnut, J. Chem. Phys. 51, 5118 (1969), and references cited therein.

[3] Z. G. Soos and D. J. Klein, J. Chem. Phys. 55, 3284 (1971).

[4] J. G. Vegter and J. Kommandeur, Phys. Rev. B 7, 2929 (1973).

[5] S. H. Khanna, A. A. Bright, F. Garito, and A. J. Heeger, Phys. Rev. B 10, 2139 (1974).

[6] T. Hibma, G. A. Sawatzky, and J. Kommandeur, Chem. Phys. Lett. 23, 21 (1973).

[7] T. Hibma and J. Kommandeur, Phys. Rev. B 12, 2608 (1975).

[8] A. Hoekstra, T. Spoelder, and A. Vos, Acta Crystallogr. B 28, 14 (1972).

[9] D. Chasseau, J. Caultier, C. Hauw, and M. Schvoerer, C. R. Acad. Sci. (Paris) C275, 1491 (1972).

[10] G. A. Sawatzky, P. I. Kuindersma, and J. Kommandeur, Solid State Commun. 17, 569 (1975).

[11] R.S. Knox, Solid State Phys. Suppl. 5, 37 (1963).

[12] R. E. Merrifield, J. Chem. Phys. 34, 1835 (1961).

[13] Y. Suezaki, Phys. Lett. A 38, 293 (1972).

[14] D. S. Acker and W. R. Hertler, J. Am. Chem. Soc. 84, 3370 (1962).

[15] L. R. Melby, R. J. Harder, R. J. Harder, W. R. Hertler, W. Mahler, R. E. Benson, and W. E. Mochel, J. Am. Chem. Soc. 84, 3374 (1962).

[16] G. T. Pott and J. Kommandeur, Mol. Phys. 13, 373 (1967).

[17] J. G. Vegter and J. Kommandeur, Mol. Cryst. Liq. Cryst. 30, 11 (1975).

[18] J. G. Vegter, T. Hibma, and J. Kommandeur, Chem. Phys. Lett. 3, 427 (1969).

[19] T. Hibma, P. Dupuis, and J. Kommandeur, Chem. Phys. Lett. 15, 17 (1972).

[20] T. Hibma, thesis (Univ. of Groningen, The Netherlands, 1974) (unpublished).

[21] P. Dupuis, S. Flandrois, and J. Neél, C. R. Acad. Sci. (Paris) C269, 1091 (1969).

[22] N. Sakai, Shiratori, and S. Minomura, Bull. Chem. Soc. Jpn. 45, 3314 (1972).

[23] P. Dupuis and J. Neél, C. R. Acad. Sci. (Paris) C265, 777 (1967).

[24] T. Hibma and J. Kommandeur, Solid State Commun. 17, 259 (1975).

[25] A. J. Silverstein and Z. G. Soos, Chem. Phys. Lett. 39, 525 (1976).

[26] M. Komo and Y. Saito, Acta Crystallogr. 30-B, 1294 (1974).