

Dynamics of triplet excitons in the simple tetracyanoquinodimethane (TCNQ) salts of rubidium, potassium, and tri-methyl-benzimidazol

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The ESR spectra of Rb^+TCNQ^- , of K^+TCNQ^- , and of TMB^+ (tri-methyl-benzimidazolium) TCNQ^- were measured. The observed dipolar splittings unequivocally prove that the ESR signals derive from triplet excitons. From the behavior of the linewidths as a function of temperature and orientation of the crystalline axes with respect to the magnetic field, the complete dynamics of the excitons can be derived. They are found to be diffusive, with hopping activation energies of 0.08 eV for Rb^+TCNQ^- and 0.16 eV for $\text{TMB}^+\text{TCNQ}^-$. The anisotropy of the exciton motion is $10^5:1$ for Rb^+TCNQ^- and $30:1$ for $\text{TMB}^+\text{TCNQ}^-$, which is in complete agreement with the crystal structures of these compounds.

I. INTRODUCTION

During the recent flurry of interest in the salts of tetracyanoquinodimethane (TCNQ) very little attention has been paid to their ESR spectra. In a number of cases these show dipolar splittings, which a decade ago already have been assigned as arising from triplet excitons.¹ These excitons can occur because of electron-electron repulsion (electron-hole attraction, Wannier excitons); because of electron-phonon coupling in a (quasi-) one-dimensional system (Peierls pairs); or as spin-wave excitations in a linear antiferromagnet. Although in view of the conducting properties of the TCNQ salts the first two interpretations would be preferred by these authors, the dynamics of the triplet excitons are quite independent of their interpretation. Moreover, since older work does not appear to have arrived at a satisfactory interpretation of the temperature dependence of linewidths and splittings, it was decided to reinvestigate these properties in Rb^+TCNQ^- , K^+TCNQ^- , and 1, 2, 3-trimethyl-benzimidazolium (TMB^+) TCNQ^- . The Rb and K salts were chosen because the TCNQ dimers line up in the usual face-to-face chainlike fashion.² In $\text{TMB}^+\text{TCNQ}^-$ salt, however, the dimers are arranged side by side.³ Schematically the two basic structures are compared in Fig. 1. Remembering that the overlap of the π orbitals is only appreciable at right angles to the benzene rings these structures should have quite different dimensionality, i.e., the Rb^+ and K^+ salts should be much more one dimensional than the TMB^+ salt.

The shapes of the triplet exciton lines in the ESR spectra of ion radical salts depends strongly on temperature. Usually the lines are very narrow at low temperature. At higher temperatures the lines broaden and shift towards each other until eventually one broad line results, which narrows at still higher temperatures. It is generally be-

lieved that the narrowness of the lines at low temperature is due to motional narrowing of the hyperfine structure, whereas the broadening and subsequent narrowing at high temperatures is due to the interaction between the triplet excitons.¹

For a localized triplet exciton one should observe the splittings due to the coupling between the electron spin and the nuclear spins (hyperfine splittings). Based on the known isotropic hyperfine coupling constants for a TCNQ^- ion radical in solution, the width of the hyperfine structure for a TCNQ^- dimer in a triplet state is expected to be about 25 MHz.¹⁵ Because the hyperfine coupling constants certainly are not isotropic, the width of this structure should depend on the orientation of the crystal with respect to the magnetic field. The very narrow lines observed at low temperatures for morpholinium⁺- TCNQ^- and triphenylmethyl-arsonium⁺- $(\text{TCNQ})_2^-$ (1-3 MHz) indicate that either the exciton is delocalized over a large number of TCNQ^- ions or the (diffusional) motion is fast compared to the hyperfine interactions. This point has received a lot of attention from Thomas,

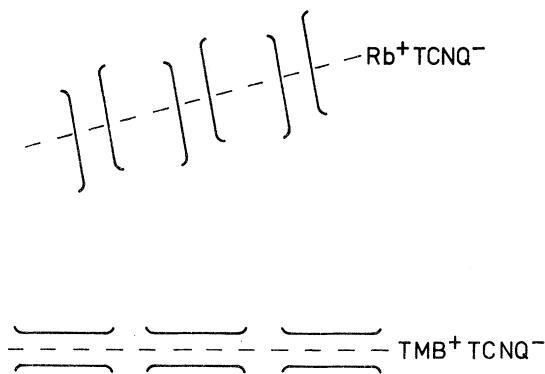


FIG. 1. Schematic structure of Rb^+TCNQ^- and $\text{TMB}^+\text{TCNQ}^-$.

Soos and McConnell,¹ and Soos.⁴ It is stated by these authors that the motion of the excitons in $[(C_6H_5)_3PCH_3]^+$ and $[(C_6H_5)_3AsCH_3]^+(TCNQ)_2^-$ is diffusional rather than wavelike. The hopping rate is sufficiently fast to narrow the hyperfine structure, but not fast enough to average out this structure completely, because the linewidth is still anisotropic. The temperature dependence of the line shape at high temperatures has been studied experimentally by Chesnut and co-workers^{5,6} for $[(C_6H_5)_3PCM_3]^+(TCNQ)_2^-$, $[(C_6H_5)_3AsCH_3]^+(TCNQ)_2^-$, $(Cs^+)_2(TCNQ)_3^{2-}$, and the simple and complex salts of morpholine and TCNQ. They assumed that the theory to describe the effect of exchange on the line shape of spin- $\frac{1}{2}$ particles applies to spin-1 particles as well. However, the theory seemed to be inconsistent with the experimental observations. The extension of the theory to spin-1 particles by Lynden-Bell⁷ apparently did not improve on this situation.

One of the discrepancies between theory and experiment is that, according to the theory, the broadening of the exciton lines should be proportional to the density of triplet excitons. However, the activation energies, as deduced from the linewidth measurements, are generally much larger than the excitation energies for the triplet excitons. Soos and McConnell¹ have suggested that the excess activation energy is due to the fact that the motion of the excitons is diffusional and thermally activated. The ions of the dimer, excited to the triplet state, tend to move apart because the binding in the triplet state is less than in the ground state. Thus a lattice distortion might lower the energy of the triplet excitation considerably and would create a barrier for the motion of the exciton. We will present some new evidence which shows clearly that the excitons in Rb^+TCNQ^- and TMB^+TCNQ^- are indeed self-trapped. Sudden linewidth changes at specific orientations of the crystals must be attributed to the jumping of the excitons between different chains of $TCNQ^-$ ions.

The hopping rate appears to be temperature activated. The activation energy for the interchain hopping rate compares well with the excess activation energy for the line broadening due to exciton-exciton interaction. An apparent discrepancy between the theory and the experimental results of Chesnut *et al.* is that the activation energy associated with the temperature dependence of the dipolar splittings is much too small compared to the value expected from theory. We will show that in the case of Rb^+TCNQ^- and TMB^+TCNQ^- the temperature dependence of the splittings at high temperatures is in agreement with the theory and that, at low temperatures, another process must be responsible.

II. EXPERIMENTAL

Details of the preparation of the materials will be published elsewhere, together with the dipolar splitting tensors and magnetic susceptibility measurements. All measurements were performed using a Varian E-3 or E-9 ESR spectrometer. The temperature dependence of the splittings was measured, using a TE_{102} cavity with two sample compartments. The magnetic field could be modulated separately at both compartments. The reference sample was a crystal of the same material as the crystal, which was investigated. This reference crystal was kept at ambient temperature. By orienting both crystals in the same way and measuring the shift of the lines of the sample, which was studied with respect to the lines of the reference sample, we were able to measure accurately the temperature dependence of the splittings.

III. INTERCHAIN MOTION OF THE EXCITON

Generally, the ESR spectrum of both Rb^+TCNQ^- and TMB^+TCNQ^- consists of two pairs of triplet exciton lines. These pairs of lines arise from triplet excitons on the two translationally inequivalent chains of $TCNQ^-$ ions.^{2,3} Because these different chains are connected to each other by a mirror plane, the chains are magnetically equivalent if the magnetic field is parallel to this mirror plane or perpendicular to it, and then only one pair of lines is observed. We noted that the linewidth is considerably reduced when the two pairs of lines coincide. This sudden change in the linewidth is due to the jumping of the exciton between the two translationally inequivalent chains, in the sense that the lines are broadened if the chains are magnetically inequivalent and they are not broadened if the chains are magnetically equivalent.

It is well known that the line shape for a spin jumping between two positions A and B is given by⁸

$$g(\nu) = \text{Im} \left(\frac{(\nu - \bar{\nu}) + i(\Gamma_A + \Gamma_B + 2\nu_t)}{[(\nu - \nu_A) + i(\Gamma_A + \nu_t)][(\nu - \nu_B) + i(\Gamma_B + \nu_t)] + \nu_t^2} \right). \quad (1)$$

ν_A and ν_B are the resonance frequencies in position A and B , respectively; Γ_A and Γ_B are the linewidths without hopping; and ν_t is the hopping frequency. In the slow-jumping limit, separate lines are observed of width

$$\Gamma = \Gamma_{A,B} + \nu_t \quad (\nu_t \ll \nu_A - \nu_B) \quad (2)$$

and a separation which is somewhat smaller than $\nu_A - \nu_B$. In the fast-jumping limit, there is only one line of width

$$\Gamma = \frac{1}{2}(\Gamma_A + \Gamma_B) + (\nu_A - \nu_B)^2 / 8\nu_t \quad (\nu_t \gg \nu_A - \nu_B). \quad (3)$$

Physically, these results may be explained as follows. In the slow-jumping limit, a spin at position A precesses around the static magnetic field with its resonance frequency ν_A . When the spin jumps to site B , it has to precess with a different frequency, leading to a phase difference with the other spins. This dephasing causes line broadening. In the fast-jumping limit, the spin has to change its precession frequency so often that, on the average, the precession is in phase with the mean resonance frequency $\bar{\nu}$. Expression (1) not only applies to spin- $\frac{1}{2}$ particles but may also be used for triplet excitons.⁹ A textbook example of the influence of the jumping of a triplet excitation between magnetically inequivalent sites on the line shape of the ESR spectrum is the triplet excitation in triptycene and tribenzotriptycene.¹⁰ Other examples are the triplet excitons in naphthalene and anthracene¹¹ and 1,4-dibromo-naphthalene.¹² In

wursters blue perchlorate,¹³ the dipolar splittings observed experimentally are characteristic for an exciton moving rapidly between two translationally inequivalent sites.

In Rb^+TCNQ^- and $\text{TMB}^+\text{TCNQ}^-$, both the slow- and fast-jumping limit are encountered at one temperature. This is shown in Fig. 2(a). If the two pairs of lines are separate and the separation $\nu_A - \nu_B$ is much larger than ν_t , according to Eq. (2), the lines are broadened by an amount ν_t . If the lines coincide, $\nu_A = \nu_B$, and the width is equal to the width it would have without hopping, according to Eq. (3). The difference between the linewidths for large and zero separation, therefore, is a direct measure of the hopping rate of a triplet exciton between translationally inequivalent chains. In this way we have measured ν_t as a function of temperature. [Note that in the case of $\text{TMB}^+\text{TCNQ}^-$ the linewidth is anisotropic, so we have to interpolate

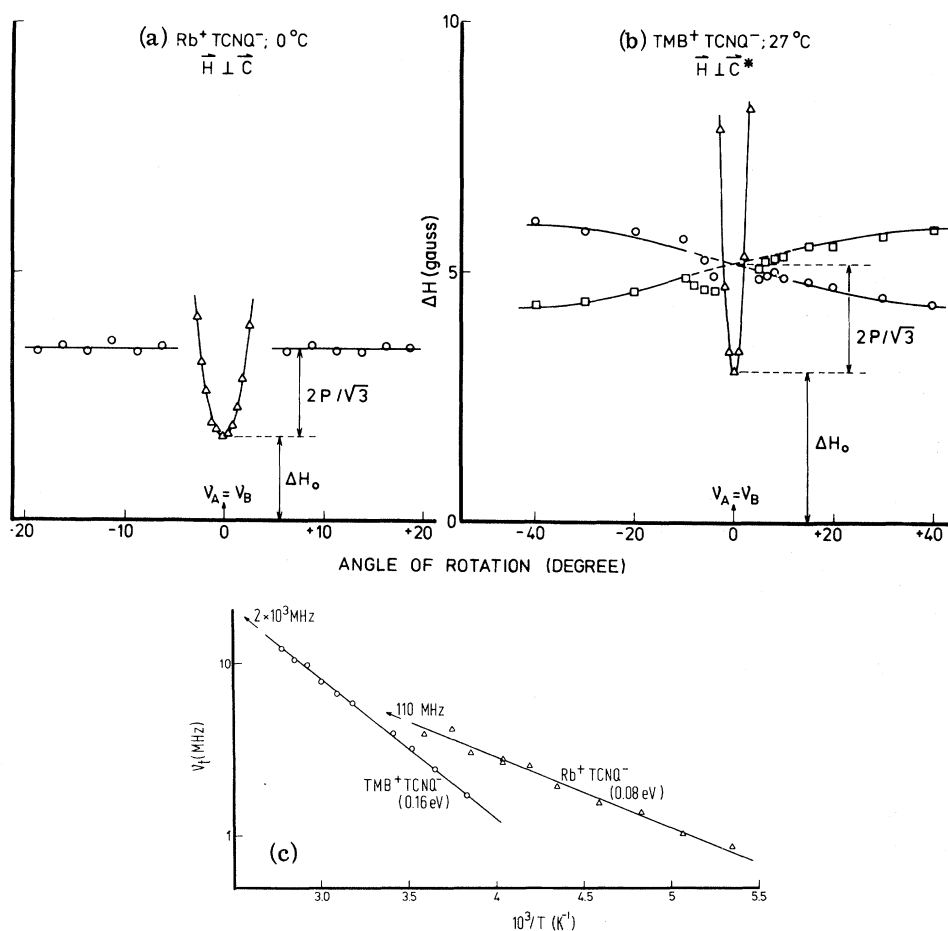


FIG. 2. (a) and (b). Width of lines due to excitons at translationally inequivalent sites as a function of the orientation of the crystal with respect to H . At angle zero the lines coincide and the linewidth is considerably reduced. Note that the width of the lines in Rb^+TCNQ^- is isotropic, whereas the width of the lines in $\text{TMB}^+\text{TCNQ}^-$ (squares and circles) is anisotropic. $P = h\nu_t/g\mu_B$ is the jumping rate in gauss. (c) Transverse jumping rate of the excitons in Rb^+TCNQ^- and $\text{TMB}^+\text{TCNQ}^-$ as a function of temperature.

the data for large separations to the point where $\nu_A = \nu_B$, as indicated in Fig. 2(b), to obtain the broadened linewidth.]

In Fig. 2(c), the logarithm of the hopping rate is shown as a function of $1/T$. It is clear from this figure that ν_t is temperature activated. The activation energies and pre-exponentials are given in Table I. The activated behavior of ν_t indicates that there is a barrier for the transport of the exciton to neighboring chains.

Therefore a lattice distortion is associated with the exciton. The height of the barrier or the trap depth will be about equal to the activation energy for the motion of the exciton. The sudden decrease of the linewidth and associated increase in height of the triplet exciton lines at certain specific orientations has also a very remarkable effect on the powder spectra of these materials (see Fig. 3). In addition to the six peaks always observed in powder spectra at resonance fields where the splittings are extreme, at $H_0 \pm D$, $H_0 \pm (D + \frac{1}{3}E)$, and $H_0 \pm (D - \frac{1}{3}E)$ (these fields are denoted by Z, Y and X, respectively, in Fig. 3) one gets six others: two where H is at right angles to the interchain mirror plane and four at positions corresponding to the extreme splittings, when H is in the mirror plane. The sudden decrease in linewidth leads to a pile-up of "intensity" there and, thus, to a peak in the derivative. The positions of the various peaks are indicated in Fig. 3; their splittings compare well with the single-crystal data, as is shown in Table II. Similar effects have been observed in the powder spectrum of 1, 2-dimethyl-3-ethyl-benzimidazolium⁺TCNQ⁻.

IV. MOTION OF THE EXCITON ALONG THE CHAIN

The lattice distortion associated with the triplet exciton will also affect the motion of the exciton along the chain. If the matrix elements responsible for the transfer of the exciton are large with respect to the self-trapping energy E_L , the motion will still be wavelike because the ions cannot follow the motion of the excitation. The distortion then is distributed over a large number of dimers. On the other hand, if the matrix elements responsible for the exciton transfer are small with respect to E_L , again, the exciton will be self-trapped and the motion will be diffusional, as in the case of the transverse motion.

TABLE I. Activation energies and pre-exponential factors of the transverse hopping rate ν_t .

	E_L (eV)	ν_0 (MHz)
Rb ⁺ TCNQ ⁻	0.08	1.1×10^2
TMB ⁺ TCNQ ⁻	0.15	2.0×10^3

TABLE II. Splittings (gauss) of the peaks in the powder spectra of Fig. 3, due to interchain hopping, as compared to the values expected from the single-crystal data.

		A	B	C
Rb ⁺ TCNQ ⁻	powder	unobs	138	128
	crystal	268	130	128
TMB ⁺ TCNQ ⁻	powder	unobs	185	108
	crystal	290	185	107

Information on the motion along the chain may be obtained from the low-temperature linewidth. Contrary to the examples mentioned in the Introduction, in both Rb⁺TCNQ⁻ and K⁺TCNQ⁻ the linewidths are isotropic over the entire temperature range studied, except for the narrowing effect described in the Sec. III. Thus any hyperfine structure has been averaged out completely, even at low temperatures.

The residual linewidth at 200°K is very small (1.5 MHz for Rb⁺TCNQ⁻ and 1.4 MHz for K⁺TCNQ⁻). Using a simple argument, it was shown by Thomas *et al.*¹ that for an exciton mov-

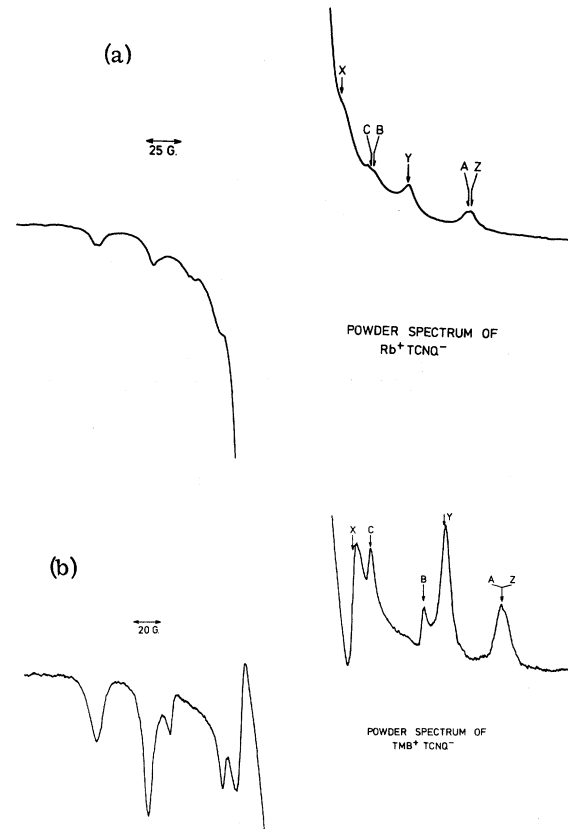


FIG. 3. (a) Powder ESR spectrum of Rb⁺TCNQ⁻; (b) powder ESR spectrum of TMB⁺TCNQ⁻.

ing in one dimension the contribution to the linewidth due to hyperfine interaction is

$$\nu_{av} \simeq (\nu_{hf}^4/\nu_j)^{1/3}. \quad (4a)$$

ν_{hf} is the width of the hyperfine structure for a localized exciton and ν_j the hopping rate along the chain. If we take 25 MHz for ν_{hf} , then the lower limit for ν_j is 10^{11} sec^{-1} . At 200°K, the hopping rate along the chain therefore is at least five orders of magnitude larger than the transverse hopping rate between translationally inequivalent chains. Soos,⁴ however, has pointed out that three-dimensional randomization processes are much more efficient in destroying the correlation between spins than the one-dimensional random walk, because in one dimension the probability that the spin returns to its original position after a jump is much higher. He showed that even if the characteristic frequency for the three-dimensional processes ν_r is some orders of magnitude smaller than the one-dimensional jumping rate ν_j , they may not be neglected in the narrowing process. He finds

$$\nu_{av} = \nu_{hf}^2 / (2\nu_j\nu_r)^{1/2}. \quad (4b)$$

Taking for ν_r the transverse jumping rate at 200°K, which is about 1 MHz, it is seen that the jumping rate along the chains should be at least 10^{11} sec^{-1} in this model, which happens to be the same value as the one obtained from Eq. (4a).

In $\text{TMB}^+\text{TCNQ}^-$ the situation is quite different. At low temperatures ($\approx 200^\circ\text{K}$) the linewidth is strongly anisotropic ($\approx 5\text{--}20 \text{ MHz}$) and much larger than in the case of Rb^+TCNQ^- and K^+TCNQ^- . The hyperfine structure has been incompletely averaged out by the motion of the exciton. At higher temperatures the anisotropy of the linewidth in absolute value disappears. This is due to motional narrowing of the hyperfine structure. One would expect not only the linewidth anisotropy to decrease, but also the linewidth itself. This is not observed because the contribution to the linewidth due to exciton-exciton interaction dominates the linewidth at high temperatures and this width increases with temperature. The hopping rate in $\text{TMB}^+\text{TCNQ}^-$, therefore, is at most of the order of the linewidth at low temperatures, i.e., 10 MHz. The theory of Soos does not apply because ν_{av} is of the same order of magnitude as ν_{hf} and the hopping rate ν_j . Theories for this limit do not appear to have been formulated. The upper limit of 10 MHz is only one or two orders of magnitude larger than the hopping rate between translationally inequivalent dimers.

Less anisotropy in the hopping rate compared to Rb^+TCNQ^- is indeed expected on the basis of

the crystal structure. The interaction between dimers in the chains is expected to be orders of magnitude smaller in $\text{TMB}^+\text{TCNQ}^-$ as compared to Rb^+TCNQ^- . The motion in $\text{TMB}^+\text{TCNQ}^-$ therefore is three dimensional rather than one dimensional.

Soos also discusses the shape of the motionally narrowed line. If the motion is slow or if the exciton motion is coherent, one would expect the lines to have approximately a Gaussian shape because then the shape would be determined by a convolution of a large number of unresolved hyperfine lines. In Fig. 4 it is shown that the line shape of the triplet exciton in $\text{TMB}^+\text{TCNQ}^-$ changes from Lorentzian at high temperatures towards Gaussian at low temperatures, consistent with the fact that the hyperfine structure is incompletely averaged out at low temperatures.

If the motion of the exciton is fast and one dimensional, the line shape should be intermediate between Gaussian and Lorentzian over the whole temperature range.

V. EXCITON-EXCITON INTERACTIONS

At high temperatures the dipolar spectra broaden and eventually collapse into one single broad line. There are a number of different possibilities to explain this behavior. Dissociation of the exciton in free electrons and holes is the first one. The second possibility is that the excitons interact with the electrons and holes present in the system. In the first case the broadening will be proportional to the dissociation rate of the triplet exciton; in the second case the broadening will be proportional to the density of electrons and holes in the system. Although contributions from these two

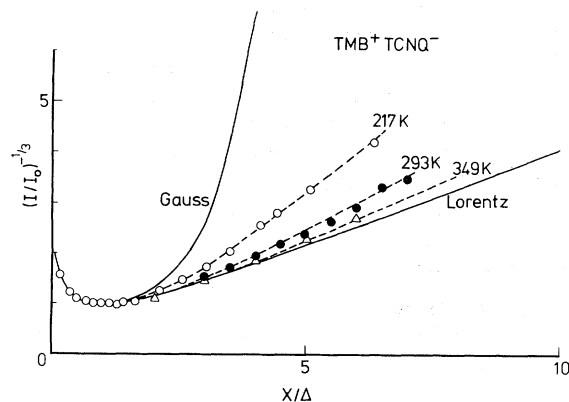


FIG. 4. Line shape of the triplet exciton line in $\text{TMB}^+\text{TCNQ}^-$ at different temperatures. The cubic root of the normalized height of the derivative of the absorption signal is plotted against the ratio of the distance to the centre of the line and one-half the difference between the extrema.

mechanisms cannot be excluded, we will show that the experimental results are in accordance with a third mechanism: broadening due to interaction between excitons.

As has been mentioned in the Introduction, this latter mechanism was proposed to be responsible for the broadening of triplet exciton spectra at high temperatures by Chesnut and co-workers.⁵ Lynden-Bell considered the line-shape problem for a system of triplet excitons interacting through exchange.⁷ We have recalculated the line shape within essentially the same model in a different, but much simpler, approach due to Zitserman.¹⁴ This calculation is presented in the Appendix. It is shown there that the results of Lynden-Bell are erroneous because she neglected important elements of the density matrix for the activated complex. In Table III, the correct results in the fast and slow exchange limit are summarized. J is the strength of the exchange coupling between two triplet excitons, τ_p is the lifetime of the activated complex consisting of two coupled triplet excitons, and τ is the mean time between successive collisions of two triplet excitons. The mean distance between n excitons on a chain of N dimers is $Na/n = a/\rho$, where a is the lattice parameter in the chain direction and ρ the density of the excitons. The mean velocity of the excitons is $\nu_j a$. Thus the mean time between successive collisions is

$$\tau = (\rho \nu_j)^{-1}. \quad (5)$$

A is the probability that a collision is effective in the relaxation process. As shown in the Appendix,

$$A = 2J^2 \tau_p^2 / (1 + 9J^2 \tau_p^2). \quad (6)$$

The parameter $J\tau_p$ is the strength of the collision. If $J\tau_p$ is large, the triplet excitons before and after the collision have the largest possible probability to be uncorrelated and A is $\frac{2}{9}$. If $(J\tau_p)^2$ is much less than $\frac{1}{9}$, the excitons are hardly affected by the collision and A (and hence the broadening) will be small. The exchange interaction in the exciton collision complex changes the spin states of the colliding triplets. Therefore, the collisions amount to an averaging of the dipolar interaction. The observed dipolar splittings will become smaller and the lines will become broader as the

TABLE III. Linewidth and splittings for a system of interacting triplet excitons (see Appendix).

	Slow exchange $A/\tau \ll d_0$	Fast exchange $A/\tau \gg d_0$
Linewidth $\Delta\nu - \Delta\nu_0$	$\frac{2}{3}\sqrt{3}(A/\tau)$	$\frac{1}{3}\sqrt{3}d_0^2(A/\tau)^{-1}$
Splittings $d_0^2 - d^2$	$2(A/\tau)^2$	0

collision frequency increases, until finally the dipolar split lines merge. Using Eq. (5), the linewidth and splittings in the slow exchange limit are

$$\Delta\nu - \Delta\nu_0 = \frac{2}{3}\sqrt{3}(\nu_j \rho A), \quad (7a)$$

$$d_0^2 - d^2 = 2(\nu_j \rho A)^2. \quad (7b)$$

It should be noted that d and d_0 are one-half the dipolar splittings.

We are now in a position to compare the experimental data concerning the high-temperature linewidths and splittings with the theoretical predictions, assuming that the temperature dependence of the line shape is due to exciton interaction. In treating the experimental data we have to be very careful, because in Secs. III and IV we have shown that there are other processes, i.e., the jumping between translationally inequivalent chains and the motional narrowing of the hyperfine structure, which contribute to the temperature dependence of the linewidths and splittings. The contribution due to the jumping between translationally inequivalent sites may be excluded by orienting the crystal in such a way that all TCNQ⁻ dimers are magnetically equivalent, i.e., if H is perpendicular or parallel to the mirror plane connecting the inequivalent sites. In this orientation we have measured the linewidths and splittings as a function of temperature for Rb⁺TCNQ⁻, K⁺TCNQ⁻, and TMB⁺TCNQ⁻. In Fig. 5, we have plotted the difference between the actual linewidth Γ and the low-temperature limiting value Γ_0 on a logarithmic scale as a function of $1/T$. Γ_0 could not be determined very accurately and was chosen within the experimental error to give the best straight line. The activation energies and pre-exponential factors (ν_0) obtained in this way are collected in Table IV.

Both the activation energy and the pre-exponential factor for TMB⁺TCNQ⁻ may be somewhat smaller because, in this case, the linewidth is probably also effected by motional narrowing of the hyperfine structure. The correction for this temperature-dependent contribution is not possible because this temperature dependence is not known. However, the correction will be small, especially at high temperatures.

According to Eq. (7a), the temperature dependence is due to ρ , A , or ν_j . If we assume the temperature dependence of A to be small, which is certainly true if the collisions are strong ($J\tau_p \gg 1$), then A is a constant ($\frac{2}{9}$). The activation energy of ρ was measured separately from the intensity dependence of the triplet signal. Subtraction leaves the excess activation energy which must be attributed to the motion of the exciton along the chains. If this motion is also governed by the self-trapping

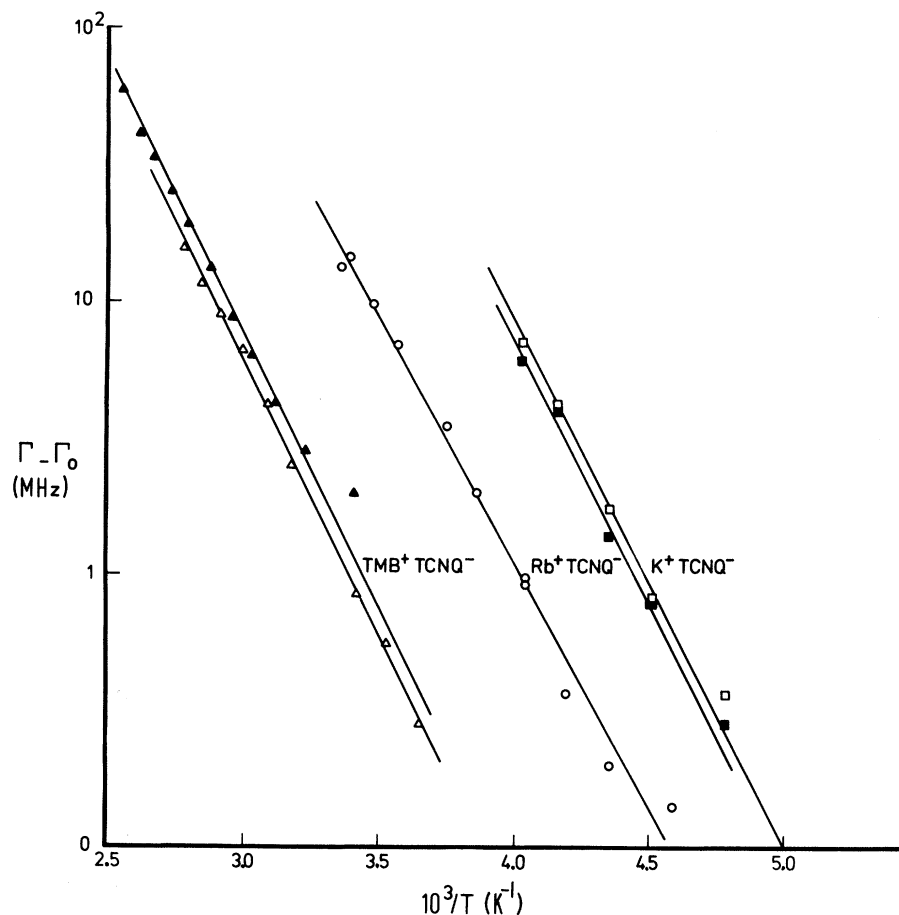


FIG. 5. Difference between the actual and low-temperature limiting values of the linewidth as a function of $1/T$ for Rb^+TCNQ^- , K^+TCNQ^- , and $\text{TMB}^+\text{TCNQ}^-$.

of the exciton, we expect this excess activation energy (E_L') to be equal to the activation energy for the interchain jumping E_L . From Table IV it is seen that the agreement between these quantities is reasonable within the experimental uncertainties. Thus it appears that the motion of the excitons along the chains is also diffusional rather than coherent. Using measured values of ρ , the quantity $\nu_j A$ may be calculated. The values of $\nu_j A$ at 200°K have been added in Table IV. In Rb^+TCNQ^- and K^+TCNQ^- , the lower limit for the jumping rate of the exciton along the chain at this temperature was determined in Sec. IV to be about 10^{11} sec^{-1} . The parameter A , which is the probability that a collision is effective in the relaxation process, therefore must be quite small (< 0.01). In

$\text{TMB}^+\text{TCNQ}^-$, however, A must be very near its maximum value ($\frac{2}{3}$) because the maximum value for ν was determined to be 10^7 sec^{-1} . Thus it is seen that the collision complex probably has a much longer lifetime τ_p in the latter case.

As pointed out before, the exciton exciton interactions should also give rise to a decrease of the dipolar splittings with temperature [Eq. (7b)]. As in the case of the linewidths, we have measured the temperature dependence of the splittings for those orientations of the crystal where the two pairs of lines due to translationally inequivalent sites coincide to exclude the effects on the splittings due to jumping between magnetically inequivalent sites. The results for two different orientations of the crystal are shown in Figs. 6 and 7 for

TABLE IV. Activation energies and pre-exponential factors for the line broadening.

	ν_0 (sec^{-1})	$\nu_j A$ (sec^{-1}) $T = 200^\circ\text{K}$	E_ρ (eV)	E_L' (eV)	E_L (eV)
Rb^+TCNQ^-	2×10^{13}	10^9	0.36	0.10	0.08
K^+TCNQ^-	3×10^{14}	2×10^9	0.38	0.13	...
$\text{TMB}^+\text{TCNQ}^-$	8×10^{12}	2×10^6	0.40	0.20	0.15

Rb^+TCNQ^- and $\text{TMB}^+\text{TCNQ}^-$. We have plotted $\log_{10}(d_0^2 - d^2)$ as a function of $1/T$, where d is one-half the actual dipolar splitting and d_0 the corresponding low-temperature limiting value. In this figure we have also drawn the curve of $\log_{10}[2(A/\tau)^2]$ vs $1/T$ as found from the linewidth measurements. It is clear that at high temperatures our data approach this calculated curve, but that at low temperature another process is responsible for the temperature dependence of the splittings. d_0 has been chosen to give the best straight line at low temperatures. The activation energy, which may be associated with this low-temperature part, has a value between 0.03–0.06 eV depending on the choice of d_0 . These values are of the same order of magnitude as the values obtained by Chesnut for $[(\text{C}_6\text{H}_5)_3\text{PCH}_3]^+(\text{TCNQ})_2^-$, $[(\text{C}_6\text{H}_5)_3\text{AsCH}_3]^+(\text{TCNQ})_2^-$, $(\text{Cs}^+)_2(\text{TCNQ})_3^-$, and Mo^+TCNQ^- . In these materials too, the temperature dependence of the splittings are most probably due to processes different from the mechanism affecting the linewidth, because the change in the splittings is much larger than the change one would expect on the basis of the linewidth data. An observation which strongly supports this idea is that $d_0^2 - d^2$ should be independent of d_0 if the change in line shape is due to the interaction between excitons. Experimentally we observe a large difference between $d_0^2 - d^2$ for two different orientations of the crystal and hence for two different values for d_0 . In fact, in Rb^+TCNQ^- $d_0^2 - d^2$ is proportional to d_0^2 . In $\text{TMB}^+\text{TCNQ}^-$ this proportionality does not hold.

One can think of two different processes which would cause this temperature dependence of the dipolar splittings. First, we point out that, if the exciton bandwidth is of the order of kT , the split-

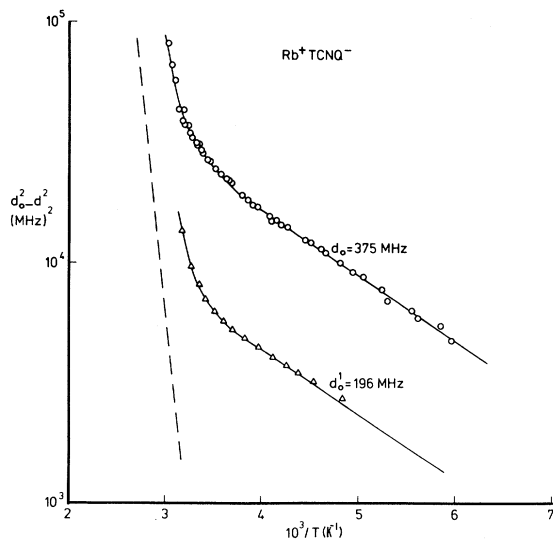


FIG. 6. $\log_{10}(d_0^2 - d^2)$ vs $1/T$ for Rb^+TCNQ^- .

tings will be temperature dependent because the splittings depend on the wave vector k . The observations in this and the preceding sections, however, strongly indicate that the effective exciton bandwidth must be very small because the motion of the exciton is diffusional rather than wavelike.

The second explanation is that the mean distance between the electron and hole increases with temperature. This might be caused by a temperature dependence of the alternation. A change in the alternation is indeed expected when the exciton density increases. Expansion of the lattice may also cause this temperature-dependent contribution. This explanation is supported by the observation¹ that the excitation energy decreases with temperature, probably due to the decrease of the intradimer transfer integral t_1 . Up to 300 °K the relative change in the dipolar splittings is about 5% for both Rb^+TCNQ^- and $\text{TMB}^+\text{TCNQ}^-$, corresponding to a change of the equilibrium distance between the TCNQ^- ions of the dimer of 2%. This is quite a reasonable value. Therefore the temperature dependence of the dipolar splittings may be viewed as an anticipation on the phase transitions in these materials. A comparison of careful temperature-dependent x-ray-diffraction measurements and dipolar splittings could be used to verify this idea. Valuable information could then be obtained concerning the nature of the Peierls transition in a one-dimensional chain.

VI. NATURE OF THE LATTICE DISTORTION

The temperature dependence of the motion of the

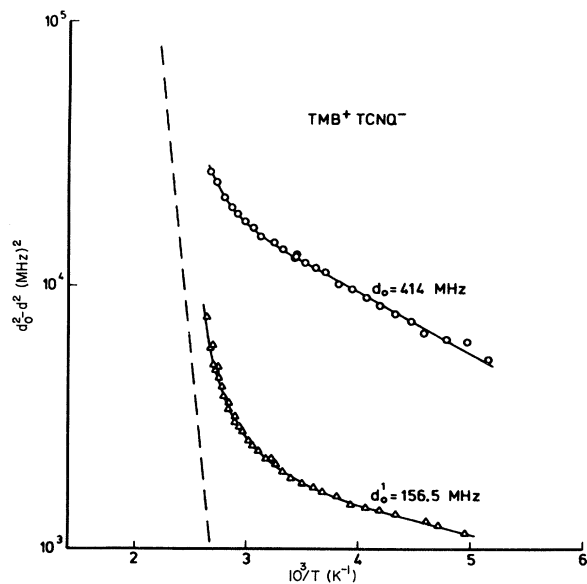


FIG. 7. $\log_{10}(d_0^2 - d^2)$ vs $1/T$ for $\text{TMB}^+\text{TCNQ}^-$.

triplet excitons, both along and between the chains of TCNQ⁻ ions, indicates clearly that the excitons are self-trapped. The nature of the lattice distortion is associated with the Peierls instability of a regular one-dimensional chain. According to Peierls,¹⁶ the chain would distort in such a way that the one-electron band splits at the Fermi level, in this way lowering the total energy of the system.

For simple TCNQ salts this argument leads to an alternating chain of ions because a band system would be half filled. The tendency towards dimerization is caused by the fact that transfer integrals increase with decreasing interionic distance and dimerization increases the possibility of electron transfer within the dimer. In the ground state the binding leads to a lowering of the energy. Obviously, this is opposed by the repulsion between the ions and the actual equilibrium positions of the ions are determined by the minimum in the total free energy of the system. For a dimer excited to the triplet state, however, electron transfer is not allowed and the driving force for the dimerization is not present anymore. The loss in lattice energy in the ground state may be recovered by increasing the separation between the ions. Thus the main feature of the lattice distortion associated with the triplet exciton is probably an increase of the separation of the ions of the dimer at which the exciton resides. In both Rb⁺TCNQ⁻ and TMB⁺TCNQ⁻, apparently, the distortion is severe enough to destroy the coherent motion of the excitons. In Rb⁺TCNQ⁻, the distortion would be in the direction of the chains, whereas in TMB⁺TCNQ⁻ the distortion would be perpendicular to the chains. It seems reasonable that the distortion in the TMB⁺ case is more severe, since in Rb⁺ and K⁺TCNQ it leads to crowding of the chain.

VII. CONCLUSIONS

In the three simple salts we studied, i.e., Rb⁺TCNQ⁻, K⁺TCNQ⁻, and TMB⁺TCNQ⁻, there are at least four different processes which influence the temperature dependence of the linewidths and/or the splittings. These contributions can be separated by a careful choice of the experimental conditions as well as a careful treatment of the

data obtained. The various components are the following:

(i) The jumping of excitons between translationally inequivalent chains leads to line broadening and changes the dipolar splittings, except for certain specific orientations of the crystals. The transverse jumping rate ν_t , determined from the line broadening, appears to be temperature activated. This process gives rise to six additional peaks in the powder spectra of Rb⁺TCNQ⁻ and TMB⁺TCNQ⁻.

(ii) The jumping along the chains manifests itself in the more or less averaging of the hyperfine structure. In Rb⁺TCNQ⁻ and K⁺TCNQ⁻, this structure is completely averaged out, whereas in TMB⁺TCNQ⁻ the inhomogeneous broadening due to hyperfine interactions is still present at low temperatures but disappears as the temperature increases.

(iii) Exciton-exciton interactions contribute to the temperature dependence of both the linewidths and splittings at temperatures where the exciton density becomes large. The line broadening is proportional to the exciton density and the velocity of the excitons. The experimental results indicate that the motion of the excitons along the chains is also temperature activated.

(iv) At low temperatures the temperature dependence of the dipolar splittings is probably due to a continuous change in the equilibrium positions of the ions. The increase of the intradimer distance is about 2% up to 300 °K.

These data clearly show that a lattice distortion is associated with the triplet exciton. This distortion is quite severe and destroys the coherent motion of the exciton. The motion of the exciton is diffusional and temperature activated. The results on the jumping rates are summarized in Table V for Rb⁺TCNQ⁻ and TMB⁺TCNQ⁻. These data demonstrate the quasi-one-dimensionality of the electronic structure of Rb⁺TCNQ.

The jumping rate along the chains is at least five orders of magnitude larger than the transverse jumping rate. In TMB⁺TCNQ⁻ the transverse and intrachain motion differ only by one or two orders of magnitude. The difference in the anisotropy of the motion of the excitons in the two salts is clear-

TABLE V. Exciton motion in Rb⁺TCNQ⁻ and TMB⁺TCNQ⁻ (jumping rates are in sec⁻¹, activation energies in eV).

	Intrachain jumping $\nu_t = \nu_{t0} \exp(-E_L/kT)$			Intrachain jumping $\nu_j = \nu_{j0} \exp(-E'_L/kT)$		
	ν_{t0}	E_L	ν_t (200 °K)	E'_L	ν_j (200 °K)	A
Rb ⁺ TCNQ ⁻	1.1×10^9	0.08	1.1×10^6	0.10	$>10^{11}$	<0.01
TMB ⁺ TCNQ ⁻	2×10^9	0.15	3.3×10^5	0.20	$\sim 10^7$	$\sim \frac{2}{3}$

ly a consequence of the different structures of the chains of TCNQ⁻ ions.

APPENDIX: INFLUENCE OF EXCITON-EXCITON INTERACTION ON THE LINE SHAPE OF THE TRIPLET EXCITON ESR SPECTRUM

Following the treatment of Zitserman,¹⁴ we will calculate the line shape of the ESR spectrum for a low-density gas of triplet excitons. We will assume that when two excitons collide they form a complex (exciton dimer) for a time τ . During this collision time a constant interaction of the form $J\tilde{S}_1 \cdot \tilde{S}_2$ couples the two triplet excitons. Without any interaction the density matrix of the colliding particles is $\rho_1 \times \rho_2$. During the time of interaction the density matrix changes to $U\rho_1 \times \rho_2 U^{-1}$, where U is the Heisenberg evolution operator

$$U = \exp(-iJ\tilde{S}_1 \cdot \tilde{S}_2 \tau_c). \quad (A1)$$

After the collision, the density matrix for one of the excitons ρ has changed to

$$\rho'_1 = \text{Tr}_2(U\rho_1 \times \rho_2 U^{-1}), \quad (A2)$$

where Tr_2 means a contraction of the 9×9 matrix to the subspace of particle 1. The equation of motion for both excitons is of the form

$$\dot{\rho}_1 = i[\rho, \mathcal{H}] + \tau^{-1}(\rho'_1 - \rho_1), \quad (A3)$$

where τ is the mean time between two successive collisions. Zitserman shows that for $S_1 = S_2 = 1$ the elements of ρ_1 are

$$\begin{aligned} (\rho'_1)_{\mu\nu} = & \sum_{\alpha, \beta, \gamma, \delta, \lambda, \lambda', s, s'} C(S\mu\lambda)C(S\alpha\beta)C(S'\gamma\delta)C(S'\nu\lambda) \\ & \times \delta_{\mu+\lambda, \alpha+\beta} \delta_{\nu+\lambda, \gamma+\delta} \Omega_{SS'}(\rho_1)_{\alpha\gamma}(\rho_2)_{\beta\delta}. \end{aligned} \quad (A4)$$

The $C(S\alpha\beta)$ are the Clebsch-Gordan coefficients for $S_1 = S_2 = 1$. S and S' are all possible total spin quantum numbers (0, 1, 2); the α, β , etc. are all possible magnetic quantum numbers for the individual spins (-1, 0, 1).

$$\begin{aligned} \Omega_{SS'} &= \langle \exp(-iJ\tau_c q_{SS'}) \rangle = (1 + iq_{SS'} J\tau_p)^{-1}, \\ q_{SS'} &= \frac{1}{2}[S(S+1) - S'(S'+1)]. \end{aligned} \quad (A5)$$

Here τ_p is the mean collision time. An exponential distribution of collision times has been assumed. If we neglect all second-order terms in $\rho \times \rho$ (all terms for which $\alpha = \gamma$ and $\beta = \delta$) there are still 90 terms left in the sum (A4). The only elements of interest for the line-shape function are ρ'_{10} and ρ'_{0-1} . After some bookkeeping we find

$$\rho'_{10} - \rho_{10} = -(\rho'_{0-1} - \rho_{0-1}) = -A(\rho_{10} - \rho_{0-1}), \quad (A6a)$$

$$A = 2\tau_p^2 J^2 / (1 + 9\tau_p^2 J^2). \quad (A6b)$$

The high-field spin Hamiltonian for the triplet exciton is

$$\mathcal{H} = g\mu_B H S_z + dS_z^2 + \mathcal{H}_t. \quad (A7)$$

d is one-half the dipolar splitting (depending on the orientation of the crystal with respect to the magnetic field H) and \mathcal{H}_t is the time-dependent Zeeman interaction with the microwave field H_1 . As usual we transform both ρ and \mathcal{H} to a rotating coordinate system in which H_1 is stationary. Using the eigenfunctions of S_z as a basis, the Hamiltonian matrix then is

$$\mathcal{H} = \begin{pmatrix} \Delta\nu + d & \frac{1}{2}\nu_1\sqrt{2} & 0 \\ \frac{1}{2}\nu_1\sqrt{2} & 0 & \frac{1}{2}\nu_1\sqrt{2} \\ 0 & \frac{1}{2}\nu_1\sqrt{2} & -\Delta\nu + d \end{pmatrix}. \quad (A8)$$

Here $\nu_1 = g\mu_B H_1/h$, $\Delta\nu = \nu - \nu_0$, and $\nu_0 = g\mu_B H/h$.

The differential equations for ρ_{10} and ρ_{0-1} then are

$$\begin{aligned} \dot{\rho}_{10} &= i[C - \rho_{10}(\Delta\nu + d)] - (\rho_{10} - \rho_{0-1})A\tau^{-1}, \\ \dot{\rho}_{0-1} &= i[C - \rho_{0-1}(\Delta\nu - d)] + (\rho_{10} - \rho_{0-1})A\tau^{-1}, \end{aligned} \quad (A9)$$

where $C = \frac{1}{2}\sqrt{2}\nu_1(\rho_{11} - \rho_{22})$ contains the strength of the microwave field H_1 and the population difference between two successive magnetic sublevels of the triplet state. The line-shape function may be obtained from (A9) under stationary state conditions ($\dot{\rho}_{10} = \dot{\rho}_{0-1} = 0$):

$$\nu(\nu) \sim \text{Im}(\rho_{10} + \rho_{0-1}) = \frac{4CA\tau^{-1}d^2}{[(\Delta\nu)^2 - d^2]^2 + 4A^2\tau^{-2}(\Delta\nu)^2}. \quad (A10)$$

Although it may be shown that the treatment of Zitserman is identical to the treatment of Lynden-Bell,⁷ her results are much more complicated. This is due to the fact that the interaction Hamiltonian she uses not only contains the exchange part, but in addition the dipolar interactions for the individual excitons. Neglecting this part of the interaction Hamiltonian is allowed if $\Lambda \ll \tau_p^{-1}$, which is very likely true. Apart from this difference between both treatments the results of Lynden-Bell are erroneous, because she neglects four elements of the 9×9 density matrix of the exciton dimer which are in fact not negligible. In her notation, these elements are the elements km , lm , $\bar{k}m$, and $\bar{l}m$. If the set of differential equations (18) in her paper is extended to include these terms, the results are identical with ours in the limit where the dipolar interaction may be neglected in the interaction Hamiltonian.

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