

## Potassium-tetracyanoquinodimethane (K-TCNQ): A spin-Peierls system

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The paramagnetic susceptibility of potassium-tetracyanoquinodimethane (K-TCNQ) as a function of temperature is analyzed. K-TCNQ is considered to be in the strong to intermediate correlation regime of the Hubbard model. The magnetic properties are described in terms of a Heisenberg exchange Hamiltonian between localized spins. The magnetic susceptibility of the high-temperature phase is fitted using the Heisenberg uniform-chain theory of Bonner and Fisher with an exchange constant  $J$  which is temperature dependent as a result of the thermal expansion along the stacking axis. The low-temperature phase is described using a nonuniform Heisenberg chain with a temperature-dependent order parameter  $\delta(T)$  having the BCS dependence as in the spin-Peierls transition. The phase transition comes from a complex displacive structural change between two locally stable overlapping modes of the  $\text{TCNQ}^-$  anions which is driven by a dimerization instability of the spin-Peierls type.

### I. INTRODUCTION

The electric and magnetic properties of organic charge-transfer salts based on the  $(\text{TCNQ})^-$  anion have been well reviewed in recent articles.<sup>1</sup> Generally speaking, they are considered as two-dimensional arrays of quasi-one-dimensional chains of  $(\text{TCNQ})^-$  anions. Of particular interest, are the properties of the alkali-TCNQ salts with full charge transfer from the metal to  $(\text{TCNQ})^-$ . In this article, we propose a spin-Peierls driving mechanism to explain the now well-observed and experimentally well-characterized high-temperature structural phase transition<sup>2-5</sup> of the alkali-TCNQ salts.

Measurements<sup>2</sup> of electrical conductivities, magnetic susceptibilities, and heat capacities of the simple alkali-TCNQ salts have revealed that phase transitions occur at  $T_c = 348, 396,$  and  $381$  K in Na-TCNQ, K-TCNQ and Rb-TCNQ, respectively. For<sup>6</sup> Na- and<sup>4</sup> K-TCNQ, both the low- and high-temperature crystallographic structures are known while for Rb-TCNQ only the low-temperature crystal structure has been determined.<sup>7</sup> The main features of the structure are face to face stacks of  $(\text{TCNQ})^-$  anions forming rows along the  $a$  axis. The interaction between the rows is weak compared to the intrachain interaction. For the three salts, the low-temperature phase shows alternation of the interplanar spacing inside the chain with a dimeric structure such that the one-dimensional unit cell contains two molecules. The lattice constant for the  $a$  direction is twice that of the high-temperature phase, where a uniform-chain structure is known to exist, at least in Na- and K-TCNQ. Magnetic susceptibilities<sup>2,16</sup> have been measured as a function of temperature and the same shape is observed for the three alkali-TCNQ salts:

exponentially decreasing small value of the paramagnetic susceptibility  $\chi$  for temperature  $T \approx \frac{1}{2}T_c$  (if contributions from paramagnetic impurities are subtracted) followed by a rapidly increasing variation for  $\frac{1}{2}T_c \leq T \leq T_c$ . For  $T > T_c$ , a gradual linear increase is observed. For these salts, the transition is first order as observed<sup>5</sup> using the temperature dependence of the intensity of the superlattice reflection below  $T_c$ . In this article, we concentrate on K-TCNQ because its structure is the best known of the group with the measured temperature dependence of the degree of dimerization, of the thermal expansion, and of the complete crystalline structure of both phases. As indicated above, the phase transition will be discussed in terms of a dimerization transition for a one-dimensional chain of  $(\text{TCNQ})^-$  anions with strong electric correlation of the charge-transferred  $\pi$  electrons.

The Hubbard model, used to treat electron correlations, has been adopted by various authors<sup>8,9</sup> as a satisfactory model to describe the behavior of the charge-transfer salts with one electron per site. The electrons can tunnel along the chains via  $\pi$  overlaps, thus providing a possible physical realization of the model, which can be written in its simplest form:

$$H = U \sum_i n_{i\uparrow} n_{i\downarrow} - t \sum_{i,\sigma} (C_{i\sigma}^\dagger C_{i+1\sigma} + C_{i+1\sigma}^\dagger C_{i\sigma}). \quad (1)$$

$U$  represents the relative Coulomb energy when a given molecular state of TCNQ [the lowest unoccupied molecular state of  $(\text{TCNQ})^0$  is doubly occupied and  $t$  is the electron-transfer integral connecting states localized on nearest-neighbor molecules.  $C_{i\sigma}^\dagger$  and  $C_{i\sigma}$  are, respectively, creation and annihilation operators for an electron of spin  $\sigma$  on the  $i$ th site, and  $n_{i\sigma}$  is the corresponding number

operator. The solutions of Hamiltonian (1) are well documented in the two extreme limits  $t \gg U$  and  $t \ll U$ . For  $t \gg U$ , electron correlations may be neglected and the electronic system can be treated in terms of single-particle band theory. This treatment leads to metallic or simple semiconducting behavior depending on whether the chain structure of (TCNQ)<sup>-</sup> is uniform or dimerized. In the opposite<sup>10</sup> strong-coupling limit,  $U \gg t$ , the electronic wave functions are localized by electron-electron repulsion and a relatively large energy gap (of the order of  $U$ ) appears in the single-particle excitation spectrum of the uniform chain. In that limit, using a perturbation expansion for the linear-chain Hubbard model with one electron per site with  $U$  as the zero-order Hamiltonian and the electron-hopping term  $t$  as the perturbation, second order gives<sup>11</sup> an effective Hamiltonian of the form of a Heisenberg spin Hamiltonian with nearest-neighbor interactions. Viewed differently, in the atomic limit, with one electron per site, each atom is occupied by one electron, and the only remaining variable in the problem is the electron spin  $\tilde{S}$ . As the overlap operator  $t$  is switched on slowly, the system remains insulating, but the spins become coupled together. Then to second order, Hamiltonian (1) reduces to

$$H = -J \sum_i \tilde{S}_i \cdot \tilde{S}_{i+1} \quad (2)$$

with the antiferromagnetic exchange interaction

$$J = -4t^2/U. \quad (3)$$

In the framework of the Hubbard model, it then becomes very important to know the magnitude of Coulomb repulsion  $U$  relative to the hopping integral  $t$  for the K-TCNQ salt. Recent experimental and theoretical results on that aspect are very indicative. Khanna *et al.*<sup>12</sup> and Tanner *et al.*<sup>13</sup> have shown that the single-particle gap (0.95 eV), as measured by optical and transport studies in K-TCNQ is much larger than that inferred from magnetic resonance measurements<sup>14</sup> for the energy (0.24 eV) of the triplet exciton. We conclude from these results that the large single-particle energy gap in K-TCNQ emerges not from Bragg reflection as in the usual band insulator with two electrons per unit cell, but directly as a result of electrons being strongly correlated. The large value of the energy gap implies that the electron-electron Coulomb repulsive interaction  $U$  is of the order of 0.9 eV, which is larger than the expected bandwidth  $t$  (of order of a few tenths of eV). K-TCNQ, then, falls into the intermediate to strong-coupling regime where the electrons are, to a large extent, localized on the TCNQ sites. Theoretical estimate<sup>15</sup> of the band and Coulomb parameters of

K-TCNQ using spin-polarized energy band structures arrives at a similar conclusion.

The magnetic properties of K-TCNQ were analyzed previously by Vegter and Kommandeur<sup>16</sup> using a one-electron semiconductor theory ( $t \gg U$ ) where the single-particle gap  $\Delta_{sp}$  results from the dimerization of a chain with a half-filled conduction band. For this band theory, the magnetic excitations are viewed as bound electron-hole pairs with an activation energy  $\Delta_M$  ( $\Delta_M \approx 0.2$  eV) equal to the single-particle energy gap  $\Delta_{sp}$ .  $\Delta_M$  is observed<sup>12</sup> to be reduced when the temperature increases towards the magnetic transition temperature  $T_c$  ( $T_c = 396$  °K). In the band model, this decrease in  $\Delta_M$  would be the result of a reduction of the single-particle gap  $\Delta_{sp}$ . In contradiction to this, microwave measurements of Khanna *et al.*<sup>12</sup> indicate that the single-particle gap  $\Delta_{sp}$  is independent of temperature in the range 77–350 °K. It is also of interest to note that in order to fit the paramagnetic susceptibility  $\chi$ , by using the band model, Vegter and Kommandeur<sup>16</sup> had to assume that the arrangement of the (TCNQ)<sup>-</sup> anions along the stacking axis was nonsymmetrical even for  $T > T_c$ . That assumption leads to a gap in the conduction band even in the high-temperature phase and was sufficient to fit the slope of  $\chi$ . However, recent x-ray investigation<sup>4</sup> showed that the high-temperature arrangement is symmetrical, leaving unexplained the proposed semiconductor-semiconductor transition of K-TCNQ in the framework of the band model. Based on these observations, we propose that the band model be abandoned for K-TCNQ.

In this article, we suggest, on the basis of the recent experimental results,<sup>4,12</sup> a different model to explain both the electronic and magnetic properties of K-TCNQ. Starting from an electronic system which is in the strong to intermediate coupling regime, we attributed the semiconducting gap, observed in both the high- and low-temperature phase, to a Hubbard correlation gap for one electron per site. However, in this quasilocated electron-wave-function limit, the spin degrees of freedom are still possible and they give rise to triplet excitons located in the single-particle gap  $\Delta_{sp}$ . The observed magnetic transition at  $T_c = 396$  °K is then attributed to a complicated distortion of the one-dimensional chain which is uniform in the high-temperature phase. This transition will be called loosely a spin-Peierls transition. One further simplification will be made by describing the magnetic system using the strong-coupling limit ( $U \gg t$ ) where the Hamiltonian may then be written as a Heisenberg Hamiltonian having alternating exchange constant  $J_1$  and  $J_2$  in the low-temperature, nonuniform dimerized phase.

In Sec. II, different physical models are reviewed to explain the weak temperature dependence of the paramagnetic susceptibility in the high-temperature phase of K-TCNQ. A realistic explanation is based on the large thermal expansion of the lattice in the  $a$  direction. Quantitative agreement is obtained using the recent measurements of the latter quantity by Konno *et al.*<sup>4</sup> In Sec. III, a model is proposed for the phase transition based on the now known detailed structural changes taking place at the transition temperature  $T_c$ . Realizing the complexity of the full description of the phase changes, a spin-Peierls-like temperature-dependent order parameter which is truncated by a displacive phase transition at  $T_c$ , is proposed to give a first-order phase transition. Using this model description, a reasonable fit for the paramagnetic susceptibility  $\chi$  is obtained in the low-temperature phase.

## II. HIGH-TEMPERATURE PHASE $T > T_c$

The paramagnetic susceptibility  $\chi$  of K-TCNQ, as a function of the temperature  $T$ , was measured first by Vegter *et al.*<sup>2</sup> using absolute EPR measurements. Their results are reproduced in Fig. 1 as the full drawn curve. The total static magnetic susceptibility of K-TCNQ crystals was measured by Laroche *et al.*<sup>17</sup> using a Faraday method from  $T = 5.4^\circ\text{K}$  to  $T = 450^\circ\text{K}$ . If the diamagnetic contribution is subtracted from the latter results, the dotted curve of Fig. 1 is obtained. (The constant-temperature diamagnetic shift was chosen for the two curves to coincide at high temperature, the values used being compatible with that obtained using Pascal rules.) The two curves coincide in a satisfactory manner over the full temperature range when account is made of the degree of precision of the measurements in the low-temperature region. In the inset, the low-temperature ( $T < 40^\circ\text{K}$ ) magnetic susceptibility is drawn from the results of Laroche *et al.*<sup>17</sup> For  $T < 40^\circ\text{K}$ , a Curie-impurity-type susceptibility is obtained, the corresponding paramagnetic impurity concentration being of one magnetic impurity for 150 TCNQ anions. For subsequent analysis, the absolute measurements of Vegter *et al.*<sup>2</sup> are used.

As indicated in the Introduction, we propose to explain the magnetic and electronic properties of K-TCNQ using an antiferromagnetic spin-exchange interaction of the Heisenberg-type between electrons well localized on their respective (TCNQ)<sup>-</sup> sites. For the general case of a nonuniform dimerized chain, the Hamiltonian for  $2N$  spins is

$$H = \sum_{j=1}^N [J_1(\vec{S}_{j,1} \cdot \vec{S}_{j,2} - \frac{1}{4}) + J_2(\vec{S}_{j,2} \cdot \vec{S}_{j+1,1} - \frac{1}{4})], \quad (4)$$

where  $\vec{S}_{j,1}$  and  $\vec{S}_{j,2}$  are the spin operators for the

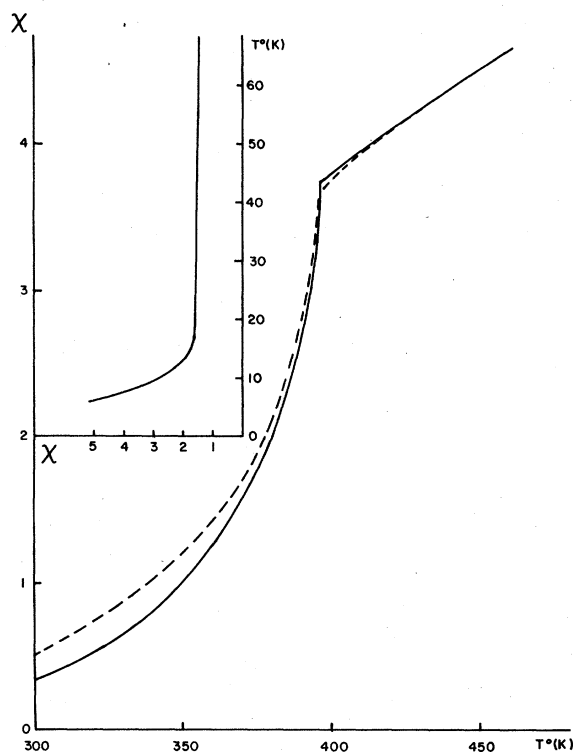


FIG. 1. Paramagnetic susceptibility per spin as a function of temperature for K-TCNQ. Full drawn line, Vegter and Kommändeur (Ref. 2); dotted line, our results. Inset, the low-temperature part of the curve.  $\chi$  is in  $10^{11}$  emu/spin with  $\mu_B\beta = 1$ .

first and second site of the  $j$ th link.  $J_1$  and  $J_2$  are the two values of the exchange parameters for the dimerized chain. They are both equal to  $J$  in the uniform chain. The best theoretical values for the magnetic susceptibility of a uniform linear chain are those of Bonner and Fisher,<sup>18</sup> obtained from an extrapolation to infinite chains of the numerical results calculated using small finite chains. Typical curves for the temperature dependence of the susceptibility  $\chi$ , obtained using the Bonner and Fisher results,<sup>18</sup> are shown in Fig. 2 for two different values of the only adjustable parameter  $J$ . Variations of the value of  $J$  only translate the susceptibility curves along the  $\chi$  axis with only a slight change of the slope. The flatness of the susceptibility for a uniform Heisenberg chain is a manifestation of the absence of a gap in its excitation spectrum and the resulting nonzero value of  $\chi$  when  $T \rightarrow 0$ . It is observed that it is strictly impossible to fit the measured susceptibility curve (full drawn curve) for  $T > T_c$  with a uniform antiferromagnetic Heisenberg chain keeping  $J$  constant.

It is possible to think of three different reasons

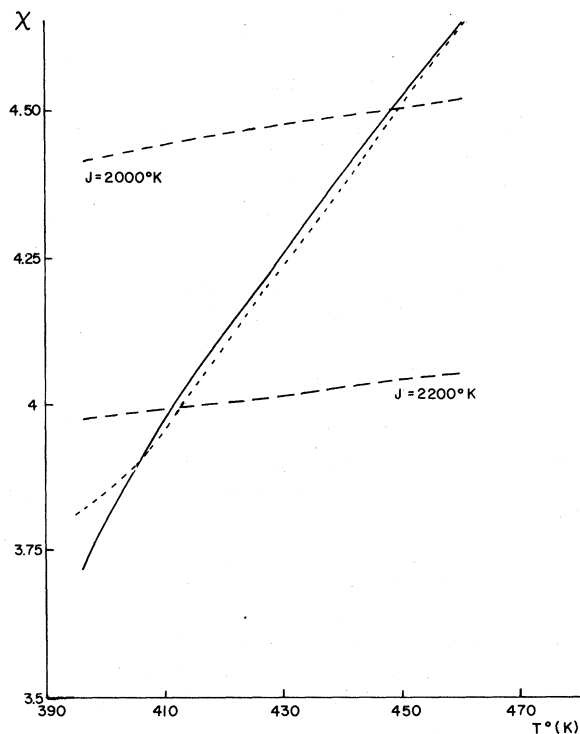


FIG. 2. High-temperature paramagnetic susceptibility per spin of K-TCNQ. Full drawn curve, experimental results (Ref. 2); the two dashed lines, uniform chain with constant  $J$  (Ref. 18); the dotted line, fit based on our model.  $\chi$  is in  $10^{11}$  emu/spin with  $\mu_B\beta=1$ .

for the Heisenberg linear chain to have a gap in its excitation spectrum with the wanted rapidly varying susceptibility for  $k_B T/J < 1$ : (a) the linear chain is dimerized (this possibility has been eliminated by the recent experimental results<sup>4</sup> for  $T > T_c$ ), (b) an anisotropy<sup>18</sup> in the Heisenberg interaction or, (c) finite chain effects<sup>19</sup> as a result of impurities and defects in the one-dimensional chain. Very small anisotropy effects are expected in K-TCNQ as indicated by EPR measurements of the  $g$  value in alkali-TCNQ.<sup>20</sup> Since an anisotropy larger than 0.5 would be necessary to explain the high-temperature results ( $T > T_c$ ), possibility (b) is rejected. As to finite chain effects (c), it is to be rejected also since chains as short as 10 (TCNQ)<sup>-</sup> anions would be necessary to obtain the desired slope, in contradiction with the very small concentration of magnetic impurities observed using the low-temperature susceptibility measurements.<sup>17</sup> We thus suppose that there is no appreciable gap in the excitation spectrum of the spin system for  $T > T_c$  and attribute the temperature dependence of  $\chi$  to variations of  $J$  as a result of the thermal expansion for a uniform one-dimensional chain.

The antiferromagnetic exchange constant  $J$  is a function of the temperature  $T$  as a result of the thermal expansion of the crystal along its  $a$  axis. In the framework of the Hubbard model,  $J$  may be written<sup>21</sup>

$$J = J_0 e^{-2bt} \simeq J_0 (1 - 2b\xi), \quad (5)$$

where  $\xi$  is the relative temperature variation of the lattice constant along the  $a$  axis and  $b$  is a parameter<sup>16</sup> characterizing the extent of the wave function. Its value depends on the type of wave function used and on the intersite distance. For K-TCNQ, it is taken<sup>16,21</sup> equal to 8. For  $T > T_c$ , the parameter  $\xi$  is defined by

$$\xi = \Delta a_{30}/a, \quad (6)$$

where  $\Delta a_{30}$  is the difference between the lattice constant along the  $a$  axis at  $T$  and its value at  $T = 30^\circ\text{C}$ . Thermal expansion is the result of anharmonic terms in the crystal potential energy giving temperature-dependent equilibrium value to the lattice constant. In relation to its thermal expansion, the K-TCNQ crystal structure<sup>4</sup> may be simply visualized as relatively soft (TCNQ)<sup>-</sup> chains supported on the perimeter by hard  $\text{K}^+$ -8N cubes also forming chains in the  $a$  direction. Each cube is formed by a  $\text{K}^+$  cation surrounded by 8 nitrogen atoms. Since these hard  $\text{K}^+$ -8N cubes linear chains are holding the crystal together, we make the reasonable assumption that the thermal expansion is not affected much by the crystal phase transition which will involve rearrangement of the (TCNQ)<sup>-</sup>s modes of overlap along the  $a$  direction. On the basis of this assumption, we estimate the thermal expansion coefficient using the value measured by Konno *et al.*<sup>4</sup> in the temperature interval  $T$  from 330 to 396°K. Their curve may be fitted with the relation

$$\xi = \Delta a_{30}/a = -1.36 \times 10^{-3} + 1.19 \times 10^{-4}(T - 303). \quad (7)$$

Substituting Eq. (7) in Eq. (5), the exchange constant  $J$  becomes

$$J_h(T) = J'_h [1 - 0.0019(T - 314.4)], \quad (8)$$

where  $J'_h$  is the only adjustable parameter and  $T$  is measured in °K. The dotted curve of Fig. 2 is obtained using the results of Bonner and Fisher<sup>18</sup> for the paramagnetic susceptibility for each value of  $J_h(T)$  determined from Eq. (8) where the only adjustable parameter  $J'_h$  is taken equal to 2700°K. From that fit,  $J_h(T)$  is seen to run from 1950°K at  $T = 460^\circ\text{K}$  to 2280°K at  $T_c = 396^\circ\text{K}$ . The fit with experimental results is excellent over the entire temperature range  $T > T_c$  with  $J'_h$  being the only adjustable parameter.

Alternatively when the one-electron tight-binding band model of Vegter and Kommandeur<sup>16</sup> is used,

the thermal expansion would affect the transfer integral as follows:

$$h = h_0 e^{-b\xi} \approx h_0(1 - b\xi). \quad (9)$$

In the framework of the one-electron band theory, using the temperature dependence of  $\xi$  from Eq. (7), the slope of the susceptibility would be roughly half what is needed to fit the experimental results. This is another indication of the failure of the one-electron band theory.

We have thus found a mechanism, to explain quantitatively the high-temperature dependence of the magnetic susceptibility, using a uniform antiferromagnetic Heisenberg interaction between localized spins and the linear thermal dependence of the exchange interaction as measured by Konno *et al.*<sup>4</sup> Only one adjustable parameter was needed, namely,  $J'_h$  which is typically 2700 °K.

### III. LOW-TEMPERATURE PHASE $T > T_c$

The low-temperature paramagnetic susceptibility of the K-TCNQ salt ( $T < T_c = 396$  °K) is now explained using a spin-Peierls mechanism coupled to a complex displacive phase transition of the quasi-one-dimensional chain of (TCNQ)<sup>-</sup> anions. K-TCNQ consists of molecules which possess internal structure and therefore the spin-Peierls transition in this quasi-one-dimensional system is more complicated<sup>22</sup> than the simple longitudinal distortion originally proposed by Beni and Pincus<sup>23</sup> and Pytte.<sup>24</sup> Fortunately, detailed crystal structure of the two phases in equilibrium at  $T_c = 396$  °K are known for K-TCNQ salt from the work of Konno *et al.*<sup>4</sup> In the low-temperature phase,  $T < T_c$ , there are two different types of chains having a dimeric structure (TCNQ)<sup>-</sup> (I) and (II) anions are inclined at angles of 15.8° and 11.3° to the plane (100), respectively. Figure 3(a) shows the overlapping modes of adjacent (TCNQ)<sup>-</sup> units in the low-temperature phase. A modified ring-ring overlap along the short axis is observed in the dimeric unit while between dimeric units there is a modified ring-ring overlap with a diagonal shift of the molecular center. For the high-temperature phase, the one-dimensional chain is uniform with the two (TCNQ)<sup>-</sup> anions becoming identical and their molecular planes making an angle of 8.9° with the (100) crystal plane. Figure 3(b) shows the overlapping mode of (TCNQ)<sup>-</sup> anions with a ring-ring overlap intermediate between those observed in the low-temperature phase. These experimental data indicate that the phase transition is displacive in character with a complicated combination of finite translation and libration motions of the (TCNQ)<sup>-</sup> anions taking place at  $T = T_c$  (the transition is a weak first-order

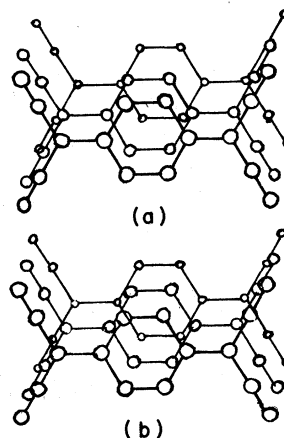


FIG. 3. Overlapping of modes<sup>4</sup> of the (TCNQ)<sup>-</sup> anions: (a) low-temperature phase; (b) high-temperature phase.

transition).

In this section, where no attempt is made to treat the detailed crystal changes taking place at the phase transition point, we present a model to describe the temperature-dependent dimerization for  $T < T_c$  which is truncated at  $T = T_c$  by a displacive phase transition. The total lattice potential energy has two metastable minima corresponding to the two different ring-ring overlapping modes of the (TCNQ)<sup>-</sup> anions along the chains. Referring to the molecular axis of TCNQ as defined in Fig. 4 and neglecting the small librational changes (rotation around the  $\xi$  axis), the lattice potential energy has two local potential wells in the  $\xi$ - $\xi$  plane. The deeper potential well corresponds to the uniform overlapping mode of Fig. 3(b) as observed at  $T > T_c$ . The other potential well, related to the former by a diagonal shift in the  $\xi$ - $\xi$  plane [see Fig. 3(a)], is

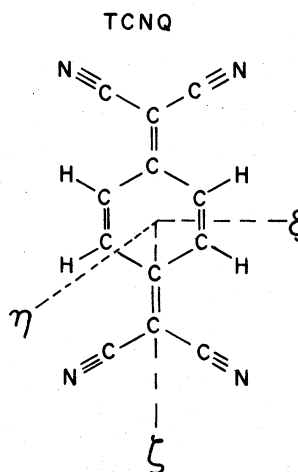


FIG. 4. Principal axis of the (TCNQ)<sup>-</sup> anion.  $\eta$  is perpendicular to the molecular plane.

not as deep as the former but is wider leading to a more easily deformable structure in the  $a$ -axis direction in this low-temperature configuration. The total free energy of the system, which includes both the lattice potential energy and the contributions from Heisenberg spin magnetic system, has its minimum for the first overlapping configuration [Fig. 3(b)] for  $T > T_c$ . As  $T$  approaches  $T_c$  from above, the local minimum of the total free energy for the second overlapping mode [Fig. 3(a)] is approaching the absolute minimum of the configuration [Fig. 3(b)]. For  $T < T_c$ , the configuration of Fig. 3(a) has a lower total free-energy minimum than configuration 3(b) and a finite dimerization, with a nonuniform chain, appears along the  $a$  direction. The appearance of a dimerized structure leads to the introduction of a gap in the quasifermion spectrum with the consequent reduction in energy. The number of adjustable parameters describing the complex crystal potential surface and their corresponding order parameters being prohibitively large, we choose not to write a formal phase transition model but describe separately the low- and high-temperature phases on the basis of the model proposed above. The high-temperature phase  $T > T_c$  has been treated in the previous section and we now concentrate on the low-temperature phase.

For  $T < T_c$ , we use the spin-Peierls theory of Pytte<sup>24</sup> which would predict a second-order BCS-type phase transition at  $T = T_c^{\text{BCS}}$ . Based on the model described above, the BCS-type dimerization order parameter in the chain direction is truncated at  $T = T_c$  when the spin-Peierls instability is coupled to the complex displacive phase transition involving translational and librational motions of the TCNQ anions. The exchange integral for the dimerized chain is written

$$J = J_1(T)[1 \pm \delta(T)], \quad (10)$$

where  $\delta(T)$  is the temperature-dependent order parameter describing the variation of  $J$  with respect to dimerization and lateral shift. We neglect the presence of the two types of chains at  $T < T_c$  in using a single expression as in Eq. (10).  $J_1(T)$  is the value of the exchange integral without dimerization for  $T < T_c$ . It depends on  $T$  as a result of thermal expansion in the same manner as expressed in Eq. (8):

$$J_1(T) = J_1' [1 - 0.0019(T - 314.4)]. \quad (11)$$

The value of  $J_1'$  is different from the value adopted for the high-temperature phase  $T > T_c$  because of the first-order displacive phase transition which has changed the overlapping modes of the (TCNQ)<sup>-</sup> anions. This is quite reasonable when we observe that the exchange constant  $J$  is a quadratic function

of the transfer integral [Eq. (3)] in the limit of the Hubbard model and that this transfer integral should be different for different modes of overlap. Assuming that the restoring force results from a quadratic form (proportional to  $\delta^2$ ) of the potential around its low-temperature minimum,  $\delta$  varies with the temperature  $T$  according to a BCS-type law<sup>24</sup> with a critical temperature  $T_c^{\text{BCS}}$ . Using this value of  $\delta(T)$ , the paramagnetic susceptibility of the dimerized one-dimensional chain is obtained from the theory of Abraham.<sup>25</sup>

Using the above model, the low-temperature susceptibility data of Fig. 1 were fitted for  $J_1' = 1800^\circ\text{K}$ ,  $T_c^{\text{BCS}} = 437^\circ\text{K}$ , and  $\delta(0)$ , the maximum value of the dimerization parameter  $\delta$  equals 0.427. The high-temperature and low-temperature fits of the paramagnetic susceptibility appear in Fig. 5. The fit is quite reasonable except near  $T = T_c$  where hysteresis effects manifest themselves for this truncated first-order phase transition. The value of  $J_1(T = 396^\circ\text{K})$  for the low-temperature phase is  $1520^\circ\text{K}$ . For  $T < 330^\circ\text{K}$ , the theoretical curve starts to deviate from the experimental results. This departure is attributed to the deviation from a quadratic dependence ( $\delta^2$ ) of the crystal lattice potential when the deformations are large (anharmonic effects). Note that the choice of the

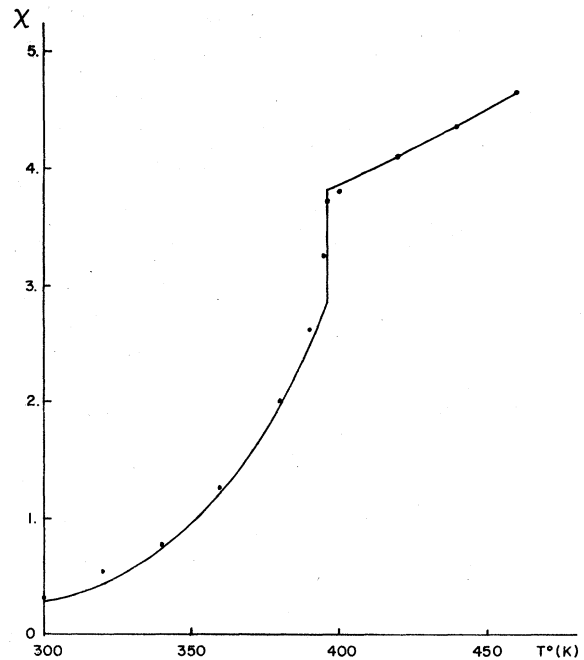


FIG. 5. Our best fit for the paramagnetic susceptibility per spin in K-TCNQ. Full drawn curve, our results; dots, experimental results (Ref. 2).  $\chi$  is in  $10^{11}$  emu/spin with  $\mu_B\beta = 1$ .

three parameters used to fit the experimental curve is not critical and that as good a fit can be obtained slightly departing from the quoted values.

#### IV. CONCLUSION

A detailed study of the paramagnetic susceptibility of  $K^+(TCNQ)^-$  shows that the temperature dependence and the phase transition are best understood in terms of a spin-Peierls instability-driven displacive structural-phase transition. In this respect,  $K^+(TCNQ)^-$  appears to fall within the limit of the strong correlation regime of the Hubbard model where the on-site Coulomb repulsion energy is considerably larger than the intersite transfer integral.

The temperature dependence of the paramagnetic susceptibility for  $T > T_c$  is explained using a uniform Heisenberg chain where the exchange integral varies with temperature as a result of the large thermal expansion of the lattice in the  $a$  direction. Using the observed thermal expansion coefficient,<sup>4</sup> the experimental results were remarkably well fitted by a single parameter ( $J'_h = 2700^\circ K$ ) theory for the entire range of temperature variations ( $396 < T < 460^\circ K$ ).

To describe the complex structural changes<sup>4</sup> appearing at  $T_c = 396^\circ K$ , a simplified displacive phase transition with a double well potential is proposed. The spin-Peierls instability, with the accompanied reduction in free energy as a result of the introduction of a gap in the excitation spectrum, is the driving mechanism for this transition. The displacive phase transition is followed by a temperature-dependent dimerized structure for the quasi-one-dimensional Heisenberg chains. The experimental susceptibility results for  $T < T_c$  are then well understood using the spin-Peierls theory of Pytte<sup>24</sup> with a BCS-type gap which is truncated at  $T = T_c$  by the displacive structural phase transition. Nevertheless, it should be mentioned that three parameters [ $J'_h = 1800^\circ K$ ,  $T_c^{BCS} = 437^\circ K$ , and  $\delta(0) = 0.427$ ] were necessary to fit the data for  $T < T_c$  and that a slightly different choice of these three parameters could fit these results equally well. Two of these parameters [ $T_c^{BCS}$  and  $\delta(0)$ ] could in principle be determined if a detailed representation of the crystal potential energy was given and if the coupling of the dis-

placive instability to the dimerization instability was written out explicitly. However, because of the complexity of the determination of the crystal potential energy from first principles, these calculations were not undertaken at this stage.

The present work suggests extensions in two different directions. First, in the framework of the Hubbard model, K-TCNQ and probably most alkali-TCNQ are known to be in the strong to intermediate correlation regime. In this work, we use for both the low- and high-temperature phases, the Heisenberg strong correlation limit of the Hubbard model. Based on the remark above, it would be interesting to see the effect of the partial delocalization of the electrons on the dimerization phase transition and on the paramagnetic susceptibility response in both the dimerized and uniform-chain structure. A second extension of the above treatment would be possible if a more detailed representation of the crystal potential was accessible. It would then become important to couple together the dimerization and displacive structural instabilities to determine their common transition temperature  $T_c$ .

In the framework of our model, it is of interest to observe that the slope of the paramagnetic susceptibility ( $T > T_c$ ) as a function of temperature,<sup>16</sup> for the alkali-TCNQ salts, increases with the mass of the alkali cations. This is compatible with our model based on thermal expansion for a high-temperature phase. In particular, for Na-TCNQ where the crystallographic structure<sup>6</sup> is well known, a similar model could be applied if the thermal expansion coefficient was measured. A further test of our model would be its applicability to the entire family of the alkali-TCNQ salts. The thermal dependence of the crystallographic structures of the other members of the family are needed to initiate such a study.

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