PHYSICAL REVIEW B VOLUME 20, NUMBER 3 1 AUGUST 1979

Low-temperature heat capacity of acridinium ditetracyanoquinodimethanide [acridinium $(TCNQ)_2$]

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(Received 18 December 1978)

The heat capacity of a high-purity sample of acridinium ditetracyanoquinodimethanide [acridinium $(TCNQ)_2$ or $Ad(TCNQ)_2$] was measured at temperatures from 0.5–10 K in fields of 0, 10, 20, and 40 kOe. The results are shown to correspond very well, within the experimental accuracy, to a superposition of a T^3 lattice contribution and a random-exchange antiferromagnetic Heisenberg-chain magnetic contribution. The Bulaevskiĭ theory parameters derived from these heat-capacity measurements without the use of any exogenous data are found to be $\alpha = 0.75 \pm 0.01$ and $A = (1.69 \pm 0.04) \times 10^{-3}\ K^{-0.25}$. The Debye temperature is found to be 68.3 ± 0.2 K.

I. INTRODUCTION

Heat-capacity measurements on a carefully purified sample of acridinium ditetracyanoquinodimethanide $[Ad(TCNQ)_2]$ at temperatures from 0.5 to 10.0 K and at fields of 0, 10, 20, and 40 kOe are reported in this paper. These measurements were carried out in an effort to clarify the low-temperature magnetic characterization of $Ad(TCNQ)_2$, and thus contribute to the understanding of the *class* of charge-transfer (CT) complexes to which this material belongs.

$Ad(TCNQ)_2$ is a *segregated*, *complex*, *regular* CT crystal.[1] The segregated designation refers to the molecular stacking, which consists of columns containing TCNQ molecules only and distinct columns containing only Ad.[2] The essentially planar TCNQ and Ad molecules are stacked face to face in their respective columns, with six TCNQ columns surrounding each Ad column. $Ad(TCNQ)_2$ is termed a complex salt because of the stoichiometry of one electron donor for each two acceptors. It is designated regular because the nearest in-stack-neighbor spacing is constant, based on room-temperature crystallographic measurements[2]. There is *no* evidence of any Peierls transition at lower temperatures (which would produce an alternation of nearest in-stack-neighbor separation, changing the designation from regular to alternating). The TCNQ units are all equivalent and, assuming total charge transfer, may be designated $TCNQ^{-1/2}$. The acridinium cations are *disordered*, according to the crystallographic results,[2] appearing in either of two alternative orientations with equal probability. Within the stacks, the interplanar separation between adjacent TCNQ's is 3.246 Å and between adjacent Ad's is 3.418 Å. The dc electrical conductivity[3] exhibits metal-like behavior at high temperatures, increasing with decreasing temperature to a maximum at 140 K. At temperatures less than 140 K it falls roughly exponentially with reciprocal temperature, like a classical semiconductor. The conductivity is highly anisotropic, with the highest-conductivity direction corresponding to the stacking direction. Measurements of the zero-field heat capacity of $Ad(TCNQ)_2$ from 0.2 to 300 K were recently reported by Delhaes, Keryer, Flandrois, and Manceau.[4] Their data will be compared with our results.

Quinolinium ditetracyanoquinodimethanide $[Qn(TCNQ)_2]$ is a segregated, complex, regular CT crystal of very similar character to $Ad(TCNQ)_2$. The Qn cations are orientationally disordered.[5] The interplanar separation between adjacent TCNQ's is 3.22 Å and between adjacent Qn's is 3.50 Å. The magnitude and temperature dependence of the conductivity are similar to $Ad(TCNQ)_2$ with the conductivity maximum occurring at about 240 K. Low-temperature heat-capacity results reported here on the Ad complex will be compared with the similar recent work of Azevedo and Clark[6] on the Qn complex.

N-methylphenazinium-tetracyanoquinodimethanide [NMP(TCNQ)] is a third high-conductivity CT salt which has often been classed with the Ad and Qn salts.[7,8] It has a 1:1 stoichiometry, making it a *simple* salt. There are at least two crystalline forms[9] which may be present in the same sample unless careful material preparation procedures are followed. Heat-capacity results currently available[10–14] are in rather sharp disagreement. Consequently, we will not make comparisons to results on this salt when discussing our data.

In these high room-temperature conductivity salts, the same donor electrons contributed by the asymmetric orientationally disordered cations are presumed to be responsible for the electrical conductivity, the paramagnetism, and the heat-capacity anomaly at low temperatures. Although this paper focuses on the interpretation of the heat-capacity anomaly, the state of understanding of the conductivity and the paramagnetism will be briefly reviewed.

In the thorough experimental study of NMP(TCNQ) by Epstein *et al.*,[15] a continuous transition from a metallic state above the conductivity maximum (200 K) to a small band-gap Mott insulator at lower temperatures was proposed to explain the conductivity behavior in the 10–300 K range. No quantitative fit of σ vs T was given. Since the conductivity versus temperature of the Ad and Qn salts is similar, the same mechanism may be invoked. A quite different interpretation was given by Bloch *et al.*,[16] who pointed out the presence of the structural disorder associated with the organic cations in the NMP, Qn, and Ad salts. Structural disorder in one-dimensional systems leads to localized electronic states. A phonon-assisted variable-range hopping mechanism was invoked to account for the conductivity between the localized states. Indeed, a quantitative theory was given which predicts a temperature dependence $\sigma \propto \exp[-(T_0/T)^{1/2}]$. This expression, for suitable choice of the constant T_0, was shown to account well for the data in a somewhat restricted temperature range below the conductivity peak, [20–60 K for $Ad(TCNQ)_2$, although over a wider range for the other materials]. At higher temperatures diffusion was invoked which leads to $\sigma \propto 1/T$, and thus may account for the decline of σ with T at higher temperatures. This hopping-diffusion theory was subsequently criticized by Ehrenfreund *et al.*,[17] who noted the unrealistic magnitudes of the experimentally determined *coefficients* of the $\exp[-T_0/T)^{1/2}]$ fits to the data.

More recently two additional theoretical descriptions of the conductivities have been given which allow rather good quantitative fits to the data over a major portion of the 10–300 K temperature range. Gogolin *et al.*[18] fit the data on $Qn(TCNQ)_2$ and acridizinium$(TCNQ)_2$ from 20–300 K using a disorder model. For $T < T_{\text{max}}$, the model attributes the increase of σ with T to hopping assisted by low-frequency intramolecular phonons. The decline in σ with $T > T_{\text{max}}$ is attributed to decreased localization associated with coupling to symmetrical intramolecular phonons and adiabatic lattice phonons. There are some questions[19] as to the appropriateness of this theory in view of the values of the (three) phonon parameters needed to achieve the fits. Epstein *et al.*[19,20] have given rather impressive quantitative fits to the data on the Ad, acridizinium, Qn, and NMP salts over the range 65–400 K. They attributed the conductivity to an activated concentration of charge carriers with a strongly temperature-dependent mobility. They accounted for the temperature dependence and magnitude of the mobility in terms of electron-phonon coupling using optical-phonon parameters which compare favorably with experimentally-determined values for TCNQ. They speculated about the origin of the energy gap which is needed to account for the temperature dependence of the carrier concentration. They pointed out that the localized states which are invoked for the disorder models are found at the band edges, but the states that dominate the σ for $T \gtrsim 65$ K are those near band center. They concluded that localized states produced by disorder may well dominate the conductivity at lower temperatures.

The static magnetic susceptibilities of the Ad, Qn, and NMP salts have been measured from 0.1 to 400 K.[21–23] ESR susceptibility measurements of $Qn(TCNQ)_2$ to temperatures as low as 30 mK have been reported.[24] For $T \gtrsim 200$ K, the paramagnetic susceptibility χ_P is *approximately* independent of temperature and has been attributed to the Pauli susceptibility of a degenerate free-electron gas, as observed in classical metals. A tight-binding one-dimensional band model gives a better fit to the observed temperature dependence of χ_P. A competing model which also fits the observed temperature dependence in this high-temperature regime is the Heisenberg linear chain model corresponding to uniform antiferromagnetic nearest-neighbor interactions along a chain of localized spins.[22] In the liquid-helium temperature range, there is a sharp rise of susceptibility with decreasing temperature. Although some have interpreted this as an impurity effect and indeed have used the Curie-Weiss law inferred from the data in the vicinity of 2–10 K to estimate the percentage of magnetic "impurities",[15,23] others have given rather convincing evidence for the intrinsic nature of the low-temperature paramagnetic rise.[21,22] Indeed, Bulaevskiĭ *et al.*[22] have shown that their data over two decades of temperature from about 0.1 to 10 K correspond to a power law in the reciprocal temperature rather than a Curie or Curie-Weiss law. They found $\chi_P \propto T^{-\alpha}$ where $\alpha = 0.74$ and 0.73 for the Ad and Qn complexes, respectively.

The earliest heat-capacity measurements on CT complexes based on TCNQ of Etemad *et al.*[9] included data on the NMP and Qn salts in the 1.5–4.4 K temperature range. The data fit nicely to a curve consisting of a linear term in T added to a T^3 lattice contribution. The linear term was attributed to magnetic interactions along the stacks between the unpaired spins corresponding to a linear Hubbard antiferromagnet. Subsequent measurements of improved resolution between 1.4 and 4.4 K on the Qn and Ad salts[23] showed clear positive deviation from this simple temperature dependence. The deviation increased with decreasing temperature, amounting to 20 or 30% at the lowest temperature measured, 1.4 K. Delhaes *et al.*[23] also measured the heat capacities of the Ad and Qn salts in high fields (to 40 kOe) and attributed the heat-capacity increase which occurred as a result of applying the field to the two-level Schottky anomalies which would result from localized spins associated with magnetic impurities. Indeed, they calculated from the Schottky anomalies the concentration of localized spins and were able to show fair agreement with a similar number obtained from the Curie constant in the magnetic susceptibility. Of course, this interpretation is in conflict with the evidence that the low-temperature paramagnetism is an intrinsic effect rather than an impurity effect. Isolated spins do not exhibit zero-field heat capacities and so the deviation from the linear term for the electronic contribution to the heat capacity is not really explained by this model.

A phenomenological theory of random exchange-coupled Heisenberg antiferromagnetic linear chains (REHAC's), with the nearest-neighbor intrachain coupling characterized by a randomly varying coupling constant, was introduced by Bulaevskiĭ *et al.*[22] to explain their susceptibility data. It predicted a susceptibility of the form $\chi_P \propto T^{-\alpha}$, in agreement with experiment. At about the same time that this theory was presented, Bloch *et al.*[16] published their disorder theory of the conductivity. Thus, both conductivity and magnetic properties were thought to be profoundly influenced by the intrinsic structural disorder in these materials.

In the REHAC theory of Bulaevskiĭ *et al.*,[22] the magnetization and heat capacity were also predicted functions of temperature and magnetic field. Magnetization measurements appeared to give results agreeing well with the theory, but heat-capacity data were not presented. A subsequent paper presented results of zero-field heat-capacity measurements on the Qn and NMP complexes from 1.5 to 5.5 K.[11] The authors fit their data and the data of Delhaes *et al.*[13] to the REHAC theory and got a good agreement with very similar parameters fitting susceptibility, magnetization, heat capacity, and high-field heat-capacity data. One point of concern with the results of some of these papers is sample purity. Little information is given on sample preparation and characterization. Is the result characteristic of the pure material or will the result vary from sample to sample depending upon the care which has been used in preparing the material? A second concern is that at temperatures above about 1.5 K where experimental data were presented, the contribution of the nonlattice term in the heat capacity is small and subject to a variety of interpretations. The temperature and field dependence of this term is much better defined if the data are extended to lower temperatures. Particularly in view of this later problem, Azevedo and Clark[6] undertook measurements to much lower temperatures of the heat capacity of $\mathrm{Qn(TCNQ)_2}$ and the authors undertook the measurements of $\mathrm{Ad(TCNQ)_2}$ reported in this paper.

II. SAMPLE PREPARATION AND EXPERIMENTAL TECHNIQUE

The crude TCNQ was synthesized according to the method of Nielsen and Carpenter,[25] and Acker and Hertler.[26] Extreme care was taken in the handling of all reagents used in the synthesis and purification of the sample. Due to the great affinity of TCNQ for metals and the deleterious effects of moisture, purification was carried out exclusively in quartz containers, and the material was recrystallized and stored under an inert atmosphere. The TCNQ was purified using the techniques of successive gradient sublimation and fractional crystallization from acetonitrile. A zone refiner for the gradient sublimation was constructed similar to the one described by McGhie, Garito, and Heeger.[27] The reagent-grade acetonitrile was purified by the method of Walter and Ramaley[28] followed by chromatography over neutral alumina and vacuum distillation over purified TCNQ.[29] Purification by other methods (two of which were tried) or the use of spectral-grade acetonitrile were unsatisfactory. Four successive purification cycles were performed on the TCNQ. Subsequent spectrophotometric analysis indicated an ionic impurity content of 10–30 ppm. Analysis of DSC (differential scanning calorimetry) gave a total impurity content of 0.02–0.03%.[30]

The crude acridine was purified by zone melting[31] and gradient sublimation. Thirty-eight passes were made with the zone-melting apparatus followed by two sublimation passes. The purity of the acridine was then determined to be 99.994% according to DSC analysis.

Synthesis of the $\mathrm{Ad(TCNQ)_2}$ was carried out in an inert atmosphere dry box at IBM San Joe Laboratories, according to the method of Melby *et al.*[32] The durohydroquinone needed for the synthesis was made by the method of James and Weissberger[33] from duroquinone and was purified by gradient sublimation. Analysis of the durohydroquinone by DSC indicated a purity of 99.968%.

The elemental analysis[34] of the final purified sample of $C_{37}H_{18}N_9$ gave 75.48% C, 3.02% H, and 21.44% N which may be compared with the expected 75.50% C, 3.08% H, and 21.42% N. After the experiments were completed, the material analyzed at 75.59% C, 3.10% H, 21.49% N.

The heat-capacity measurements were performed on a 649 mg cylindrical pill which was compressed at a pressure of 13 000 psi and was greased with about 5 mg of Apiezon "N" to copper plates contacting the plane surfaces of the sample, one of which supported the manganin heater and the other the Ge and carbon resistor sensors. Measurements were performed using the conventional heat-pulse technique in an adiabatic calorimeter using a ^{3}He evaporation cryostat which has been described in earlier publications.[35]

The calorimeter system was checked for accuracy by measurement of a 10 g sample of National Bureau of Standards copper test-specimen material. Over the measurement temperature range from 0.8 to 10 K, our data were in excellent agreement with the "copper reference equation" of Osborne, Flowtow, and Schreiner.[36] The standard deviation of the data from the reference equation was 1.5% and the average deviation was 0.2%.

A superconducting solenoid provided the magnetic field for the high-field measurements, with an estimated field accuracy and homogeneity of 1%. The temperature sensors at high fields were $\frac{1}{8}$-W Allen-Bradley carbon composition resistors. These were calibrated in zero field against the germanium sensor and then corrected to appropriate high-field resistance values using the $\Delta R/R$ data obtained on similar resistors by Sample *et al.* and Neuringer and Shapiro.[37] The carbon sensors were recalibrated during each experimental run at from 20 to 30 points. Two different resistors were used to cover the appropriate temperature range. In the regions of overlap of the different resistors, the data from different resistors agreed to within expected experimental error. Independent direct calibration of the sensors at selected temperatures gave $\Delta R/R$ values in excellent agreement with the published results. The points were fitted to calibration curves which were typically 5 to 8 parameter Chebysheff polynomial power series for log T as a function of log R. The number of parameters (order of the polynomial) was determined by the criteria discussed by Collins and Kemp.[38]

III. RESULTS AND INTERPRETATION

The measured zero-field heat capacity as a function of T from 0.5 to 10 K is shown in Fig. 1. The data have been corrected for the measured addenda. The correction amounted to 49% at 0.5 K, 62% at 1 K, 54% at 2 K, 49% at 4 K and 38% at 10 K, and was measured in a separate experiment.

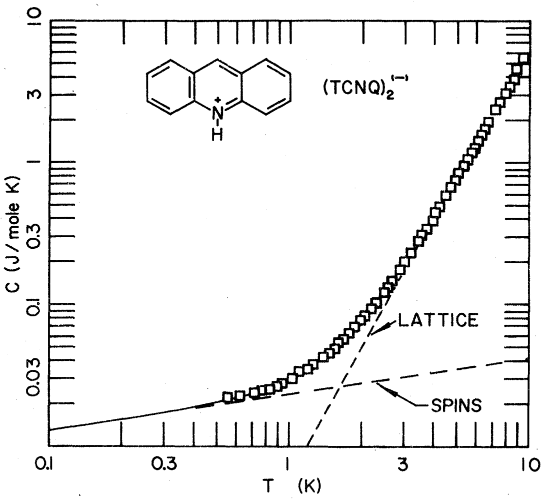

FIG. 1. Zero-field heat capacity of Ad$(TCNQ)_2$ vs temperature. The squares are experimental data points; some have been omitted for clarity of presentation. The spin and lattice contributions to the fit of Eq. (5) are shown as dashed lines. The total least-squares fit curve, which is visible at the low temperatures, corresponds to $(23.2 \pm 0.2)T^{0.25} + (6.10 \pm 0.02)T^3$ mJ mole^{-1} K^{-1}.

The results of heat-capacity measurements in fields of 10, 20, and 40 kOe are displayed in Fig. 2. This graph shows plots of

$$\Delta C(T,H) = C(T,H) - C(T,0) \ ,$$

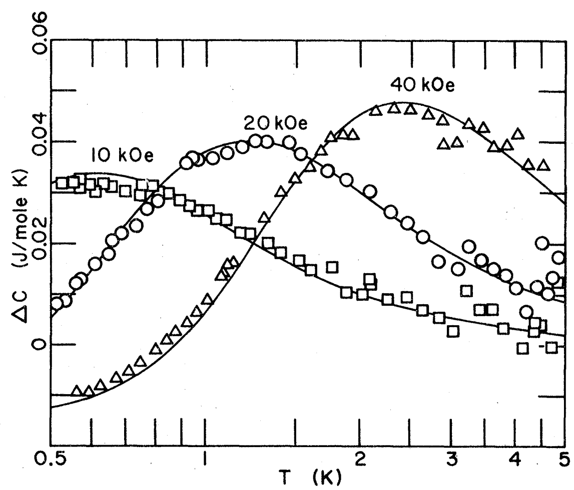

FIG. 2. Incremental heat capacity $\Delta C(T,H) = C(T,H) - C(T,0)$ of Ad$(TCNQ)_2$ vs temperature, for magnetic fields of 10, 20, and 40 kOe. The curves correspond to Eqs. (3) and (4), with parameters $\alpha = 0.75 \pm 0.01$ and $A = (1.69 \pm 0.04) \times 10^{-3}$ K$^{-0.25}$.

the heat-capacity increment resulting from the application of a magnetic field H, as a function of T, from 0.5 to 5 K. These *difference* data have been corrected for a small measured field-dependent addenda correction which is at most 7% (at the highest field and lowest temperatures).

A quite satisfactory interpretation of the experimental data has been achieved by application of the REHAC theory of Bulaevskiĭ *et al.*[22]. Bulaevskiĭ considers a regular antiferromagnetic linear chain of spins ($S=\frac{1}{2}$) coupled to nearest neighbors via Heisenberg exchange by a *random* interaction parameter. He approximates this system via a Landau-Fermi-liquid theory by a system of Fermi quasiparticles of energy ϵ with a density of states function, $\rho(\epsilon)$, given by

$$\rho(\epsilon)=\frac{A}{k^{1-\alpha}|\epsilon|^{\alpha}} , \tag{1}$$

where α and A are parameters to be determined by experiment, and k is Boltzmann's constant. The motivation for choosing this particular singular form of ρ was that it yielded the observed temperature dependence of the magnetic susceptibility,[22] proportional to $T^{-\alpha}$ with $0<\alpha<1$. Given the form (1), Bulaevskiĭ *et al.* have calculated the free energy, internal energy, heat capacity, magnetization, and susceptibility of the REHAC system. The heat capacity in zero field, $C_{\mathrm{Bu}}(T,0)$, is given by

$$C_{\mathrm{Bu}}(T,0)=[(2-2^{\alpha})\Gamma(3-\alpha)\zeta(2-\alpha)ANk]T^{1-\alpha} , \tag{2}$$

where Γ is the gamma function, ζ is the Riemann zeta function, and N is the number of spins in the chain. The increase in heat capacity with applied magnetic field, which is a more sensitive function of field than the heat capacity itself, is given by

$$\begin{aligned}\Delta C_{\mathrm{Bu}}(T,H)&=C_{\mathrm{Bu}}(T,H)-C_{\mathrm{Bu}}(T,0)\\&=ANk\left(\frac{g\mu H}{k}\right)^{1-\alpha}f_{\alpha}(t) ,\end{aligned} \tag{3}$$

where g is the electron g factor, μ is the Bohr magneton, and $f_{\alpha}(t)$ is a dimensionless function of the dimensionless variable $t=2kT/g\mu H$. The integral form for this function,[39]

$$f_{\alpha}(t)=t^{-2}\int_0^{\infty}x^{-\alpha}\left[\left(\frac{1+x}{\cosh\frac{1+x}{t}}\right)^2+\left(\frac{1-x}{\cosh\frac{1-x}{t}}\right)^2-2\left(\frac{x}{\cosh\frac{x}{t}}\right)^2\right]dx , \tag{4}$$

may readily be evaluated numerically, with the aid of a computer. The function $f_{\alpha}(t)$ given by Eq. (4) is zero at $t=0$; as t increases from zero it monotonically decreases to a minimum, then increases monotonically through zero to a single *positive* maximum, then monotonically decreases to zero as t approaches ∞. Apart from a constant factor, the heat-capacity increment *at constant field*, as given by Eq. (3), has the same dependence on T as does f_{α} on t. The value of $t=t_{\max}$ where the function $f_{\alpha}(t)$ has its maximum is approximately one and very insensitive to α. The magnitude of $f_{\alpha}(t_{\max})$ is quite sensitive to α, however, varying from 1.02 at $\alpha=0.6$ to 3.08 at $\alpha=0.8$. The heat-capacity increment ΔC_{Bu} at the temperature of its maximum is similarly sensitive to α, if α is considered as the only adjustable parameter.

Mindful of this sensitivity of the heat-capacity increment to the value of α, we fit the value of the maximum of the 20 kOe experimental curve shown in Fig. 2 to the theoretical maximum value given by Eq. (3). Depending on our choice of $0<\alpha<1$, different values of the parameter A were obtained. We chose to fit to the 20 kOe curve, since it has the most clearly defined and accurately determined maximum. Thus, from the heat-capacity increment data, we obtained a one-to-one set of values of α and A. The zero-field molar heat-capacity data, as shown in Fig. 1, were then fit to a curve of the form

$$C(T,0)=H_1T^{1-\alpha}+H_2T^3 , \tag{5}$$

where H_1 is the constant coefficient of the presumed REHAC term, corresponding to the bracketed part of Eq. (2); H_2 is the constant coefficient of the lattice term. An excellent least-squares fit of the zero-field data to Eq. (5) was achieved for a range of values of α from about 0.6 to 0.9. The corresponding values of H_1 change only about 4%. From H_1, the value of A may be calculated using Eq. (2) for the given α, which value is also insensitive to α. If we then require that the value of A which is appropriate to the incremental heat-capacity peak for a certain α should also be appropriate to the zero-field curve of Eq. (5) with the same α, the value of α is rather accurately determined to be 0.75 ± 0.01. The uncertainty is small because the curve of A vs α for the incremental peak fit has a large negative slope, while the curve of A vs α for the zero-field fit has a small positive slope, thus permitting an accurate determination of the point of intersection.

Using the data from 0.5 to 5 K and $\alpha=0.75$, the coefficients in Eq. (5) are found to be

$$H_1=22.8\pm0.8\ \mathrm{mJ\ mole^{-1}K^{-1.25}}$$

and

$$H_2 = 6.06 \pm 0.02 \text{ mJ mole}^{-1}\text{ K}^{-4} .$$

Appreciably different coefficients are obtained if the data from 5–10 K are included in the fit. A weighted fit[40] which is believed to be more appropriate, gives much better agreement with the higher-temperature data included. The weighting factor used was equal to the reciprocal squared heat capacity, based on the experimental observation that to a good approximation the *fractional uncertainty* in the heat-capacity data is constant, independent of T. With the weight factor, the least-squares coefficients are

$$H_1 = 23.3 \pm 0.2 \text{ mJ mole}^{-1}\text{ K}^{-1.25}$$

and

$$H_2 = 6.10 \pm 0.02 \text{ mJ mole}^{-1}\text{ K}^{-4} ,$$

derived from the data from 0.5–10 K. Using these coefficients, values of $A = 0.001\,69 \text{ K}^{-0.25}$ and $\Theta_D = 68.3$ K are obtained. The smooth curves shown in Figs. 1 and 2 were calculated using these parameters and $\alpha = 0.75$.

IV. DISCUSSION

The heat-capacity results of this work are compared with results of other authors on both $Ad(TCNQ)_2$ and $Qn(TCNQ)_2$ in Table I. The zero-field data in each case has been fitted to Eq. (5). The A value was determined from H_1 and Eq. (2); the Debye temperature Θ_D was determined from H_2, assuming $\Theta_D = (1944/H_2)^{1/3}$. In most cases, as may be seen, we have made the zero-field data fit using the value of α determined from the susceptibility data of Bulaevskiĭ *et al.*[22] This was done since it is impossible to obtain an accurate value of α from zero-field C data above 1.5 K in these materials. In two cases, using the data of Delhaes *et al.*,[23] it was possible to use the procedure of evaluation from ΔC data which we used with our results allowing a determination of *all three parameters* from heat-capacity data alone. We hope that the respective authors will pardon us for putting our own estimates of error limits on the parameters determined from their data, based on the scatter in published data displays.

First, we should indicate that our zero-field data agree with the data of Delhaes *et al.*[23] to within about 2% over the 1.4–4.4 K range, and to within experimental error below 2 K. Their incremental data at 40 kOe exhibits a peak at the same temperature of the same magnitude as ours, to within the experimental error.

The incremental heat-capacity anomalies shown in Fig. 2 have been attributed to Schottky anomalies[23] associated with the interaction of localized isolated "impurity" spins with the external field. Two prominent features of the curves of Fig. 2 contradict this assumption. First, the maximum value of $\Delta C(T,H)$ is independent of field for a two-level Schottky anomaly, in clear disagreement with the data. Second, there is no possibility of negative values of $\Delta C(T,H)$ at sufficiently low temperatures for a Schottky curve, as is clearly evident from the 40 kOe data. Both features are expected in the REHAC theory.

The recent paper of Delhaes, Keryer, Flandrois,

TABLE I. Results of heat-capacity measurements on $Ad(TCNQ)_2$ and $Qn(TCNQ)_2$.

Material	T range K	H values kOe	α	α estimator	10^3A $K^{\alpha-1}$	Θ_D K	Reference
$Ad(TCNQ)_2$	0.5–10.0	0,10,20,40	0.75	ΔC_{max} & C	1.69 ± 0.04	68.3 ± 0.2	This work
	1.4–4.4	0,40	0.74	χ of Ref. 22.	1.82 ± 0.11	68.7 ± 0.5	23
			0.73	ΔC_{max} & C	1.80 ± 0.08	68.7 ± 0.5	
	0.2–300	0	0.74	χ of Ref. 22.	2.22	68.3	4
$Qn(TCNQ)_2$	1.7–4.2	0	0.73	χ of Ref. 22.	0.45 ± 0.28	71.9 ± 1.9	10
	1.4–4.4	0,20,40	0.73	χ of Ref. 22.	1.61 ± 0.11	76.8 ± 0.5	23
			0.72	ΔC_{max} & C	1.59 ± 0.08	76.8 ± 0.5	
	1.5–5.5	0	0.73	χ of Ref. 22.	1.5 ± 0.1	75 ± 1	11
	0.07–5	0–20	0.82	χ of Ref. 24.	1.81 ± 0.1	78.4	6
	1.5–4.2	0	0.73	χ of Ref. 22.	1.95 ± 0.18	72.8 ± 0.6	13
	1.5–4.2	0	0.73	χ of Ref. 22.	1.82 ± 0.18	73.2 ± 0.7	13 (recrys.)

and Manceau[4] corresponding to the last $\mathrm{Ad(TCNQ)_2}$ entry in Table I appears to contain the results reported in the earlier publication of Delhaes, Aly, and Dupuis[23] between 1.4 and 4.4 K, augmented by additional data at lower and higher temperatures. The curve below 1 K is appreciably flatter than given by our data, yielding a value of $C(0.5,0)$ about 50% larger than our results. The corresponding fit to Eq. (5) over the range 0.2–5 K is poor. Although parameter values are given in Table I for the "best fit", the resultant curve simply does not accurately reproduce the data, even for α as large as 1.

In summary, three out of the four determinations of the model parameters on $\mathrm{Ad(TCNQ)_2}$ are in excellent agreement with the REHAC model, with parameters that agree to within experimental error. The agreement is also excellent with the susceptibility determination of $\alpha = 0.73$ of Bulaevskiĭ *et al.*[22] and our heat-capacity determinations of α (0.75 for our data and 0.73 for Delhaes *et al.*[23] data). The A value of $(1.9 \pm 0.1) \times 10^{-3}\ \mathrm{K}^{\alpha-1}$, determined from the 0.1–10 K χ_P data and the very low-temperature magnetization[22] measurement, appears to be slightly higher than given by the thermal results. Just how many independently prepared samples are involved in the $\mathrm{Ad(TCNQ)_2}$ entries of Table I is not clear; there are at least two and possibly three. Of course, there is the additional sample synthesized by the Russian group[22] for their χ_P and M measurements.

The Qn data represent the work of five groups, with presumably five independently prepared samples. The REHAC theory curves fit the data rather well in all cases, although out of the six data sets only those of Refs. 6 and 23 involve sufficiently low-temperature or high-field data to serve as *critical* tests of the correctness of the theory, to the exclusion of other interpretations which have been suggested. The parameter values of these two groups clearly do *not* agree. This may be just a result of variations in the degree of randomness of the quinoline orientation in different crystals of the material, as is suggested by the susceptibility measurements on different $\mathrm{Qn(TCNQ)_2}$ samples by Tippie and Clark.[24] More surprising, however, is the discrepancy reported by the authors of Ref. 6 between the susceptibility determination of

$$A = (1.03 \pm 0.11) \times 10^{-3}\ \mathrm{K}^{\alpha-1}$$

and the heat-capacity determination on the same sample of

$$(1.81 \pm 0.1) \times 10^{-3}\ \mathrm{K}^{\alpha-1} \ .$$

More measurements on well characterized $\mathrm{Qn(TCNQ)_2}$ samples at low temperatures and in high fields would help to clarify the interpretation.

Most authors[10,13,23] have reduced their 1.5–5 K zero-field data assuming equations of the form

$$C(T,0) = \gamma T + \beta T^3 \ ,$$

or

$$C(T,0) = \gamma T + \beta T^3 + \delta T^{-2} \ ,$$

on the assumption that the T term is from electronic or magnetic linear chains and the T^{-2} term accounts for impurities. Based on such measurements on $\mathrm{TTF(TCNQ)_2}$,[41] it was suggested that sample impurities increase the γ and the Θ_D derived from the β in both the Ad and Qn salts. This does not appear to be supported by the recent measurements of Kondow *et al.*[13] on $\mathrm{Qn(TCNQ)_2}$, which are referenced in the last two entries of Table I. Their recrystallized sample showed the same γ's (12.6 ± 0.5 vs 12.6 ± 0.2 mJ $\mathrm{mole^{-1}\,K^{-2}}$) and a 4% *higher* Θ_D (when evaluated from β, not H_2), as compared to the unrecrystallized material. It may also be inferred that the sample of Ref. 10 was very "different" from the other measured Qn samples. It had a γ of 5.0 ± 2.5 mJ $\mathrm{mole^{-1}\,K^{-2}}$ compared to values ranging from 12.2–12.7 mJ $\mathrm{mole^{-1}\,K^{-2}}$ on the other five measured $\mathrm{Qn(TCNQ)_2}$ samples which are listed in Table I. There is no evidence that this sample was the "purest" or "best characterized". It appears to have an abnormally low γ which would imply low impurity content if one accepts the hypothesis of large γ corresponding to large impurity content.

The linear chain Hubbard Hamiltonian has often been applied to the system of charge-transferred electrons on the stacked electron acceptor molecules in the CT crystals. In a series of papers, Theodorou and Cohen[8,42–46] have developed a theory of the *disordered* Hubbard chain which they apply to the charge-transferred electrons on the TCNQ stacks in the Ad, Qn, and NMP salts. They have started from the Hubbard Hamiltonian

$$\begin{aligned}\mathcal{H}_{\mathrm{Hu}} = \sum_{i,s} \epsilon_i a_{is}^{\dagger} a_{is} + U \sum_{i} a_{i\uparrow}^{\dagger} a_{i\uparrow} a_{i\downarrow}^{\dagger} a_{i\downarrow} \\ + t \sum_{i,s} (a_{is}^{\dagger} a_{i+1,s} + a_{is}^{\dagger} a_{i-1,s}) \ ,\end{aligned} \tag{6}$$

where the $a_{is}^{\dagger}$ and a_{is} are the usual electron creation and annihilation operators, the ϵ_i are the single-site energies considered to be random variables with uniform probability distribution of width W, U is the Coulomb repulsion, and t is the transfer integral. On the assumption that $t << W$, U, Eq. (6) was shown by Theodorou and Cohen[42,46] to reduce at low temperatures to an antiferromagnetic Heisenberg Hamiltonian characterized by a nearest-neighbor spin-spin interaction parameter J which is a random variable. This corresponds to localized electron states. The probability distribution of J is proportional to $J^{-\alpha}$ where $0 < \alpha < 1$. The probability distribution of J has this singular character only in one dimension.

According to this model, $\chi_P \propto T^{-\alpha}$ and $C(T,0)$ varies as $T^{1-\alpha}$. These results are found to hold for arbitrarily filled bands and an arbitrary amount of charge transfer. The Bulaevskiĭ *et al.*[22] and Theodorou-Cohen models clearly have significant common features, notably the predicted temperature dependence of the theromdynamic properties. The two theories have been compared by Theodorou.[44]

Calculations of charge transfer have been made based on assumed linear variations of certain carbon-carbon bond lengths[5,47] in $TCNQ^{-s}$ with s, the number of electrons transferred to each TCNQ. Using this approach, one finds $s = 0.13 \pm 0.26$ for $Qn(TCNQ)_2$. The crystallographic data[2] on $Ad(TCNQ)_2$ are not sufficiently precise to make such a determination. If the s value for the Ad and Qn complexes is appreciably different from 0.5, one would expect a contribution to the thermodynamic properties from the REHAC's on the cation stacks as well as from the TCNQ stacks. Different values of the Hubbard parameters and different amounts of band filling would likely lead to different values of the exponent α for the two stacks. This would lead to a superposition of thermodynamic functions for the two and a more complicated temperature dependence than given, e.g., by Eq. (5). No such behavior has been observed experimentally.

ACKNOWLEDGMENTS

The authors wish to acknowledge the invaluable help of Terry Manchester, Carol Michelson, and Kathleen Haas with various aspects of this work. We appreciate the advice on sample purification from Dr. Andrew McGhie and Dr. Paul Nigrey of the University of Pennsylvania. We are indebted to Dr. Ed Barrall, Miss Anne Gregges, and Dr. Richard Larrabie of the IBM Research Laboratory (San Jose). The work was supported in part by the NSF under Grant No. DMR 73-07650.

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[30] The DSC analysis was kindly carried out at the IBM San Jose Laboratory by Dr. Ed Barrall and Miss Anne Gregges.

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