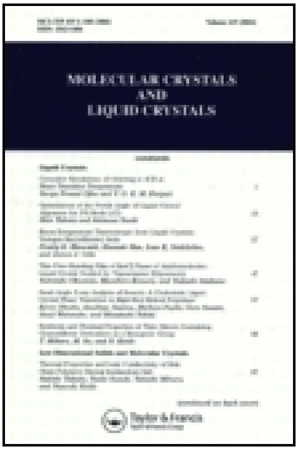

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# Comparative Esr Studies of Solid Polycrystalline Alkali Metal Salts of Tcnq and Tcnqf$_4$

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# COMPARATIVE ESR STUDIES OF SOLID POLYCRYSTALLINE ALKALI METAL SALTS OF TCNQ AND TCNQF$_4$

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Abstract The results of comparative ESR studies of the polycrystalline salts of alkali metal TCNQ and TCNQF$_4$ are presented. The temperature dependence of the relative magnetic susceptibility as determined by ESR techniques is presented. All the TCNQ salts studied show a thermally activated paramagnetism, whereas, at least, one of the TCNQF$_4$ salts follows Curie Law. The principal components of the g-tensors have been measured as a function of temperature. There is considerably more variation in both sets of measurements from alkali metal to alkali metal for the salts prepared from TCNQF$_4$ than there is for those prepared from TCNQ.

## INTRODUCTION

ESR studies of dilute solutions of KTCNQ and KTCNQF$_4$, in our laboratory, have demonstrated that both anion radicals are ion paired in solutions of ether type solvents. The proposed structures for the ion pairs are different for the two different radical ions[1]. This structural difference arises because the total charge density distribution in the two anion radicals is considerably different due to the strong electron withdrawing fluorine atoms of TCNQF$_4$.

A more recent study, in our laboratory, of the physical and spectroscopic properties of the solid state potassium salts of TCNQ and $TCNQF_4$ shows that the two salts do not possess isomorphous crystal structures[2]. A review of the literature shows considerable variation in the crystal structures when $TCNQF_4$ is substituted for TCNQ in the preparation of charge transfer complexes from a given donor(See references 1 and 2). Also observed is a discontinuous change in the ESR spectral envelope of polycrystalline $KTCNQF_4$ at 150 K. Based on our ESR study of the polycrystalline salts of KTCNQ and $KTCNQF_4$, we have discovered what may be a general and relatively quick technique to screen polycrystalline charge transfer salts for the existence of low lying thermally activated exciton states.

Thus, a comparative ESR study of the entire alkali metal series of solid state TCNQ and $TCNQF_4$ anion radical salts has been initiated, a preliminary report of which is presented here. The reasons are several fold. One, to see if the differences between KTCNQ and $KTCNQF_4$ are paralleled in the balance of the alkali metal series. Two, to determine what effect, if any, the heavy alkali metal ions(Rb and Cs) have directly(i.e., because of their larger spin orbit interaction engeries) upon the g-tensors of their respective salts. Three, since, in general, excitonic solids possess many of the same electronic and crystalline properties as possessed by low dimensional conductors, it was of interest to further test our newly discovered technique for screening for excitonic solids.

## EXPERIMENTAL TECHNIQUES

The $TCNQF_4$ was prepared as described in Ref. 3 and TCNQ was purchased from Aldrich Chemical Co. The alkali metal $TCNQF_4$ and TCNQ salts were prepared from the appropriate precursors following the procedure described in the literature for the respective alkali metal TCNQ salts[4].

The the details of the ESR spectrometer and the experimental techniques used in the studies described here are discussed elsewhere[1,2] and will not be repeated here.

## EXPERIMENTAL RESULTS

### TEMPERATURE DEPENDENCE OF ESR SPECTRAL INTENSITIES

The experimental study of the temperature dependence of the ESR spectral intensities(i.e., the magnetic susceptibility) is of considerable significance because it provides insight as to the electronic and magnetic properties of the systems under study. For example, many charge transfer salts and complexes display activated ESR magnetic susceptibilities and many of these are observed to be exciton solids in which the planar paramagnetic species present in the complex are stacked pancakewise. Thus, based only on an ESR study of the temperature dependence of the magnetic susceptibility of a series of polycrystalline solids, one can make a limited judgement as to which materials might be so structured in the solid state. This information when combined with an ESR study of the spectral envelopes as a function of temperature can be very useful as a rather definitive screen for excitonic solids[4]. Table I summarizes the results of our studies on the alkali metal TCNQF$_4$ salts and provides a comparison with the results for the corresponding TCNQ salts taken from the literature. The temperature range used for the study of the TCNQF$_4$ salts was 110 to 300 K with exception of KTCNQF$_4$ which has been studied from ~4.2 to 300 K.

It is interesting to note that all of the alkali metal TCNQ salts display activated(i.e., low lying excited) paramagnetic states with a narrow range of activation energies[4] whereas, one of the alkali metal salts of TCNQF$_4$ follows Curie law(i.e., LiTCNQF$_4$).

TABLE I Summary of Activation Energies, J, in ev. for Alkali Metal TCNQ and $TCNQF_4$ Salts.

| Ratio M:T | Metal | TCNQ | $TCNQF_4$ |
|---|---|---|---|
| 1:1 | Li | 0.10[a]<br>0.23[b] | Curie Law[f] |
| 1:1 | Na | - | Curie Law[f,g] |
| 1:1 | K | 0.21[c]<br>0.24[d] | 0.053[h] |
| 1:1 | Rb | 0.29[b] | ~0.053[f] |
| 1:1 | Cs | - | 0.042[f] |
| 2:3 | Cs | 0.16[e] | - |

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[f] This work.

[g] Spectra show the superposition of two thermally activated species.

[h] M. T. Jones, S. Jansen, A. Berndt, S. Puloka, R. D. Rataiczak and D. J. Sandman, In Preparation.

## ESR SPECTRAL ENVELOPES OF POLYCRYSTALLINE SAMPLES

The ESR spectral envelopes of polycrystalline alkali metal TCNQ and TCNQF$_4$ salts have been studied as a function of temperature for most of the possible alkali metal TCNQ/TCNQF$_4$ pairs.

Figure 1 shows a plot of the values of the principal components of the g-tensor for polycrystalline LiTCNQF$_4$. As Table I shows this material obeys Curie Law over the temperature range of the study. Hence, the spin concentration is independent of temperature as is the ESR spectral envelope as shown in Figure 1. It is also of interest to note that the polycrystalline ESR spectral envelope is symmetrical in contrast to the spectral envelope of LiTCNQ which is asymmetrical.

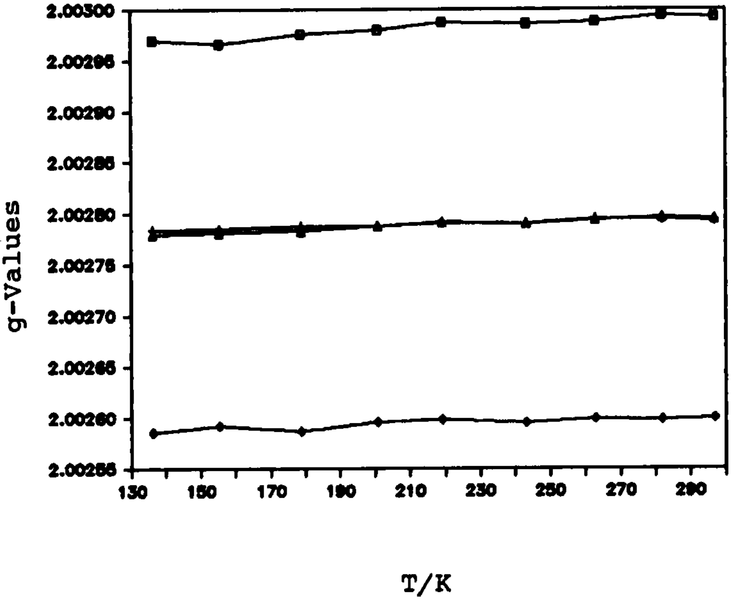

Figure 1 Plot of the values of the principal components of the g-tensor for LiTCNQF$_4$ as a function of temperature where $g_1$ = squares, $g_2$ = +'s, $g_3$ = diamonds, and <g> = triangles.

Figure 2 shows several spectra taken as a function of temperature for the $NaTCNQF_4$ salt.

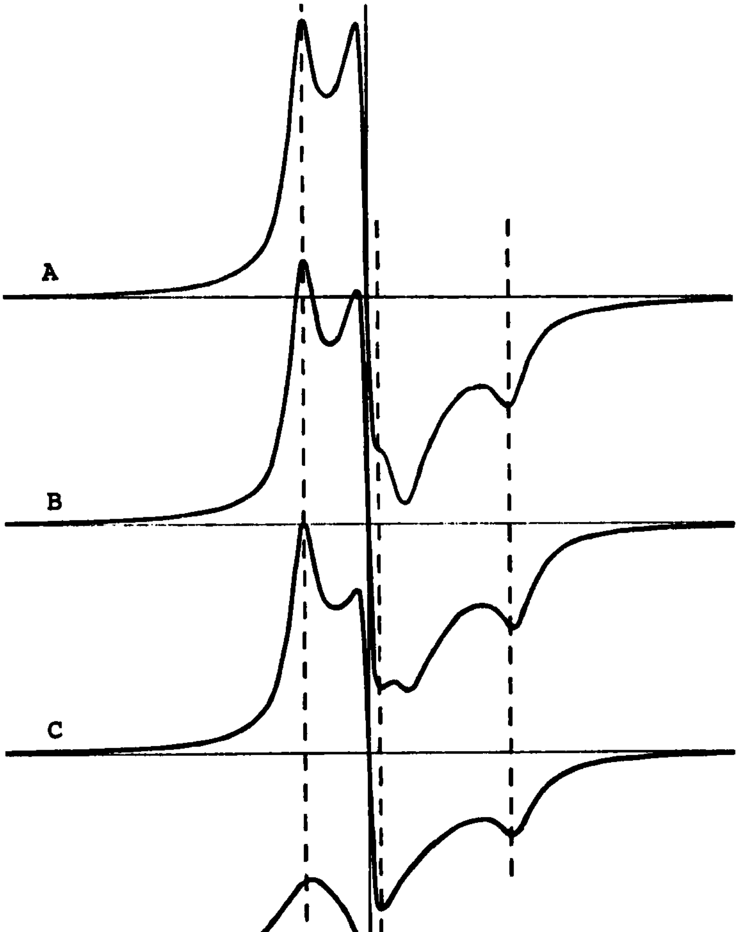

Figure 2 ESR spectra of $NaTCNQF_4$ as a function of temperature where A = 237 K, B = 227 K, C = 212 K and D = 161 K.

The NaTCNQF$_4$ salt at room temperature displays a complicated spectrum at room temperature which appears to be the superposition of two spectra both of which arise from thermally activated paramagnetic species. As the temperature is lowered the intensities of both spectra decrease. However, one decreases more rapidly than the other. We are working on the problem of deconvolution of these spectra in our laboratory.

The ESR spectral envelope of polycrystalline KTCNQF$_4$ is strongly temperature dependent and undergoes an abrupt change at *ca* 150 K(See Ref.2). A number of charge transfer salts are known to undergo crystalline phase transitions as a function of temperature(e.g., KTCNQ[2,5] and triphenylmethylphosphonium(TCNQ)$_2$)[6]. In many instances, these phase transitions are reflected in changes in the observables of an ESR experiment(e.g., the g-tensor, magnetic susceptibility, spectral linewidth, etc.). The rather dramatic change in the ESR spectral envelope as a function of temperature for KTCNQF$_4$ raises the question as to whether this might be due to a such a phase transition. This question remains unanswered at the moment, however, a number of physical studies are underway in an attempt to provide the answer.

The RbTCNQF$_4$ salt appears to behave in a fashion similar to that of the KTCNQF$_4$ salt.

Figure 3 shows a plot of the values of the principal components of the g-tensor for CsTCNQF$_4$ as a function of temperature. Two things are of interest. First, there is a significant narrowing of the spectral linewidth as the temperature is lowered. Second, the spectra are symmetrical as they are for LiTCNQF$_4$.

The values of the principal components of the g-tensors were measured from the spectral envelopes using the method of Kneubul[7]. Values so obtained at room temperature are shown in Tables II and III. One is struck by the fact that in the

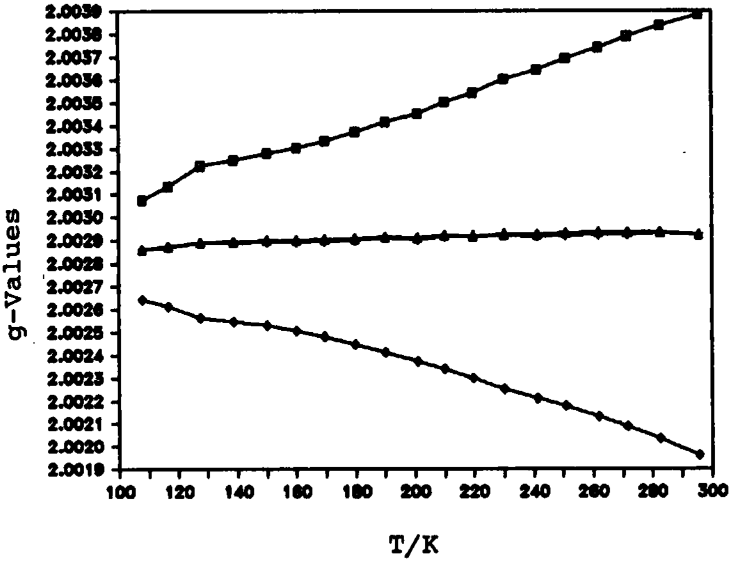

Figure 3 Plot of the values of the principal components of the g-tensor for $CsTCNQF_4$ as a function of temperature where $g_1$ = squares, $g_2$ = +'s, $g_3$ = diamonds, and <g> = triangles.

TCNQ series all the spectra are symmetrical(i.e., $g_2$ = <g> with the exception of those observed for the Li(1:1) and Cs(2:3) salts. In the $TCNQF_4$ series, the K and Rb(1:1) salts display asymmetrical spectra. These differences are under active investigation.

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TABLE II Room Temperature g-Tensors for Alkali TCNQ Salts

| Salt | $g_1$ | $g_2$ | $g_3$ | <g> |
|---|---|---|---|---|
| 1:1 Salts | | | | |
| Li | 2.002762 | 2.002678 | 2.002409 | 2.002616 |
| Na | 2.002896 | 2.002734 | 2.002558 | 2.002729 |
| K | 2.002861 | 2.002703 | 2.002543 | 2.002699 |
| Rb | 2.002869 | 2.002615 | 2.002375 | 2.002619 |
| 2:3 Salts | | | | |
| Cs | 2.004171 | 2.003237 | 2.002359 | 2.003256 |

TABLE III Room Temperature g-Values for Alkali TCNQF$_4$ Salts

| Salt | $g_1$ | $g_2$ | $g_3$ | <g> |
|---|---|---|---|---|
| 1:1 Salts | | | | |
| Li | 2.002993 | 2.002793 | 2.002600 | 2.002795 |
| Na | - | - | - | - |
| K | 2.003078 | 2.002902 | 2.002508 | 2.002829 |
| Rb | 2.003106 | 2.002850 | 2.002546 | 2.002834 |
| Cs | 2.003884 | 2.002925 | 2.001962 | 2.002924 |

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