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Charge transfer and ionic bonding in organic solids with segregated stacks

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In ionic charge-transfer salts which have segregated stacks of organic donor (D) and acceptor (A) molecules, the major feature of the classical electrostatic interactions is the strong repulsion between like charges along the stacks. Two ways are described by which the magnitude of this repulsion may be decreased: (i) by the formation of a complex salt (i.e., one whose ratio $D:A \neq 1:1$); and (ii) by incomplete transfer of charge from D to A. In both cases, some of the molecules in the stack are neutral, giving rise to a mixed-valence, partly ionic ground state. The first effect is quantitatively investigated by a Madelung energy calculation of tetrathiafulvalene-$Br_{0.79}$ as a function of (theoretical) bromine concentration. The results of this calculation show that the unusual composition of this salt occurs in order to reduce the Coulomb repulsion along the stacks. As an example of the second effect, a similar calculation is described for TTF-TCNQ (tetrathiafulvalene-tetracyanoquinodimethane), as a function of the amount of charge transferred from TTF to TCNQ. Although electrostatic interactions do not give a complete description in this case, they are clearly an important factor in determining the degree of charge transfer in such salts. In fact, in cases where the net electrostatic binding energy is small, incomplete charge transfer may be energetically favored. In this case, the charge distribution is shown to be modulated along the stack and charge density waves are formed, with wave vector "$4k_F$". These results are compared to the case of Rb-TCNQ, where the Madelung energy is shown to favor complete charge transfer.

I. INTRODUCTION

Considerable work has recently focused on attempting to understand the unusual electronic and magnetic properties of the quasi-one-dimensional charge-transfer salts[1,2] of TCNQ (tetracyanoquinodimethane). These properties generally reflect the behavior of electrons which are transferred from a donor [e.g., TTF (tetrathiafulvalene)] to an acceptor (e.g., TCNQ), and hence require the formation of a stable ionic (charge transferred) ground state of the molecular crystal. Since the ionization potential I of the donor is generally several electron volts higher than the electron affinity, A, of typical organic acceptors, charge transfer often does not occur between molecules in solution[3] and the vast majority of donor-acceptor crystals have nonionic ground states.[2] Hence, it is of interest to understand just how an ionic ground state is stabilized in the small number of known ionic crystals. McConnell, Hoffman, and Metzger[4] have suggested that the ground state will be ionic if the Madelung energy E_M gained by forming the ionic structure is sufficiently large to offset the cost ($I-A$) of ionizing the lattice; i.e., $|E_M| > I-A$. This simple rule of thumb has been used by Metzger[5] to compare the energies of two *non*ionic and two ionic donor-acceptor crystals with alternating stacks, i.e., stacks with donor and acceptor molecules alternating along the stack (as opposed to *segregated stacks*, where there are separate stacks for donors and for acceptors).

In the case of charge-transfer salts with segregated stacks, the Madelung energy E_M^F has been calculated (assuming full charge transfer) for a few of the simple salts of TCNQ (i.e., those with 1:1 stoichiometry) (Table I). For Na-TCNQ and the two phases of Rb-TCNQ, Metzger[6] and Vegter and Kommandeur[7] have shown that $|E_M^F|$ is greater than $I-A$ by ~3 eV per molecule, as expected for a strongly bound ionic solid. Similar calculations (Table I) for[8-11] TTF-TCNQ and NMP-TCNQ (NMP, N-methylphenazinium),[12] however, reveal that $|E_M^F| < I-A$ and hence, according to the simple rule of thumb, it is not clear why the ground state in these crystals is ionic. Thus, this initial work indicates the need for additional studies of the binding in these charge-transfer salts.

The major point of the present paper[10] is to describe two qualitatively new consequences of the electrostatic binding in salts with segregated stacks. These two features are particularly important for determining the electronic properties of charge-transfer salts of TCNQ.[13] In some cases a significant reduction in the classical Coulomb repulsion between charges along the stacks may be achieved: (i) by relaxing the restriction of a full (single) electron transfer from donor to acceptor (i.e., allowing incomplete charge transfer); or (ii) by relaxing the restriction of forming only salts with a 1:1 composition. Both of these possibilities will then result in less than one unpaired electron per TCNQ molecule and a partly ionic, mixed-valence stack of molecules. The first pos-

TABLE I. Properties of some simple TCNQ salts (assuming full charge transfer).

Salt	No. stacks/100 Å^2	E_M^F	$I-A$[a]	E_M^F+I-A
Na-TCNQ	2.7	−5.29 eV (Ref. 6)	2.3 eV	−3.0 eV
Rb-TCNQ (I)	2.5	−4.71 (Ref. 6) −4.85 (Ref. 7)	1.4	−3.3
Rb-TCNQ (II)	2.8	−4.64 (Ref. 6)	1.4	−3.2
NH_4-TCNQ	2.6	−4.82 (Ref. 6)		
Morpholinium-TCNQ	2.4			
TTF-TCNQ	1.8	−2.3 (Ref. 8−11)	4.05[b]	+1.7
NMP-TCNQ	1.6	~0 (Ref. 12)	3.7[c]	+3.7
"TTF-$Br_{1.0}$"	3.3	−3.9	3.3[b]	−0.6
TMPD-I	4.1	−4.27 (Ref. 53)	3.1	−1.2

[a] $A = 2.8$ eV for TCNQ (Refs. 6, 55).

[b] $I = 6.85$ eV for TTF (Ref. 43).

[c] $I = 6.5$ eV for NMP (Ref. 57).

sibility has been independently proposed by Klymenko *et al.*[11] in their very recent discussion of ionic binding in TTF-TCNQ. In addition, we suggest that this mixed-valence structure could well be responsible[13,14] for the relatively high conductivity observed for TTF- and NMP-TCNQ compared with Na- and Rb-TCNQ. Concerning the second point, a large variety of complex salts (i.e., those whose stoichiometry is not 1:1) of TCNQ have been found.[1,2,15] The halide salts of TTT (tetrathiotetracene)[16] and[17-21] TTF are also often halide deficient (see Sec. II), the latter being metallic at room temperature.[22-26] We suggest that these complex salts tend to be formed (rather than the simple 1:1 salts) in order to reduce the Coulomb repulsion along the stacks, as we shall describe.

Before getting into the bulk of the paper, we want to clearly state our major assumption explicitly: we shall assume that the transfer (or resonance) integral t associated with the delocalization of the electrons down the chain is much smaller than the Coulomb interactions between molecules. This assumption is based upon estimates[1,2] of ~0.1 eV for t compared to estimates[9] of, for example, ~2 eV for the Coulomb repulsion between two neighboring TCNQ molecules in TTF-TCNQ. For the purpose of making the electrostatic binding energy calculations tractable, we shall consider the extreme limit of this assumption, in which we regard the electronic wave function, *not* as delocalized and extended over all molecules, *but* as extending primarily over one molecule. This localization is presumably driven by electron-electron interactions,[27] which are assumed not to be strongly screened. Thus, we view the molecules as *either* singly charged or neutral, but not doubly or fractionally charged. Evidence for some degree of charge localization has come from optical[14] and[28] ESCA (electron spectroscopy for chemical analysis) measurements, although an alternative interpretation of the ESCA measurements[29] as well as evidence against such charge localization have also been given.[30] The small size of t combined with the low electron density (~2×10^{21} cm^{-3}) in these materials further suggest that the Coulomb interactions will tend to cause the electrons to form an ordered charge lattice or Wigner crystal.[31] The very recent discovery[32,33] of diffuse x-ray scattering at "$4k_F$" has been interpreted[27,34,35] as evidence for Coulombically driven charge-density waves, which in the extreme limit of strong interactions correspond[27,34] to the Wigner crystal. Such an extreme model of an ordered lattice of charges is used to model the charge distribution, largely for calculational ease, and is discussed further in Sec. V. In any case, the calculations presented here represent an examination of the interesting consequences of such a Wigner crystal in a solid with segregated stacks. The apparent success of these calculations, particularly for the case of TTF-$Br_{0.79}$, implies that the above assumptions have some validity.

In these charge-transfer salts, the planar organic molecules generally stack face-to-face in separate donor and acceptor stacks along the z axis.[36] These become positive and negative ions if a full charge is transferred between them, giving rise to a structure similar to that shown schematically in Fig. 1. It is useful to view the structure as consisting of sheets of charge normal to the stacking axis (z). The electrostatic binding *within* a sheet is attractive since the sheets contain ions of opposite charge. The electrostatic interaction *between* sheets, however, is strongly repulsive, since it is dominated by the close in-

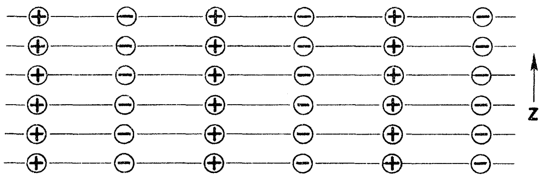

FIG. 1. Schematic structure of charges in a salt with segregated stacks and complete charge transfer.

teraction between ions with the same charge. We suggest that, in some cases, it might be energetically favorable if some of the molecules in the stack were neutral. The ground state of this system would then be mixed valence, with both neutral and singly charged molecules along the stack. The average spearation z between the charges along the stack would be larger than the separation z_0 between neighboring molecules, and the repulsion along the stack would be reduced. There are at least two possible origins of neutral molecules in the stack: (i) incomplete charge transfer from donor to acceptor; and (ii) deviation from 1:1 stoichiometry. Examples of these two possibilities are shown schematically in Figs. 2(b) and 2(c). These should be compared with the schematic representation of the usual 1:1 case with full charge transfer, shown in Fig. 2(a).

In Secs. II–VI, calculations will be described which illustrate just how the Coulomb repulsion along the stacks can be reduced in the two ways mentioned above. In Sec. II, we will describe calculations which suggest why the compound TTF-$Br_{0.79}$ forms with that particular composition. This compound represents an interesting case in which the charge transfer is complete due to the strong electronegativity of the halide ion. The reduction in the electrostatic repulsion of like charges along the stack is then achieved by the formation of a nonstoichiometric salt. In Sec. III, TTF-TCNQ is discussed, and it is shown how the Madelung repulsion can be reduced due to the formation of a mixed-valence ground state arising from incomplete charge transfer. In Sec. IV we discuss the rule of thumb criterion mentioned above and the relation of it and our calculations to the stability of the ionic crystal. The importance of a modulated charge density along the stack is described in Sec. V. In conclusion, Sec. VI contains a description of how the amount of charge transfer is related to the Madelung energy.

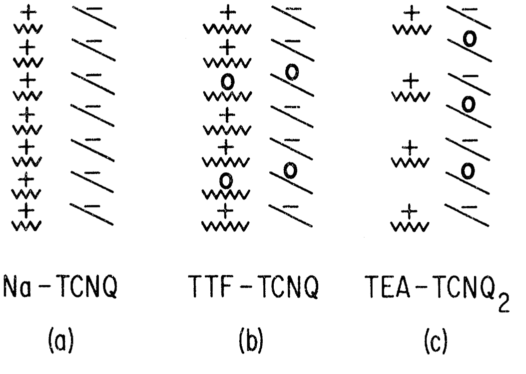

FIG. 2. Schematic structures of three types of ionic charge-transfer salts with donor (ww) and TCNQ (⧵) molecules: (a) simple salt with complete charge transfer; (b) simple salt with incomplete transfer; and (c) complex salt.

II. SALTS WITH A DEVIATION FROM 1:1 COMPOSITION

Perhaps the clearest example of the reduction of Madelung repulsion by the formation of a complex salt (i.e., one whose stoichiometry is not 1:1) is the bromide salt of TTF. The structure of this highly conducting compound [metallic, with $\sigma \sim 400$ $(\Omega\ \mathrm{cm})^{-1}$ at[20,22,26] 300 °K] has been determined by La Placa *et al.*[18] The crystal contains an equal number of stacks of Br and TTF molecules, as indicated by the view down the stacking axis (c axis) shown in Fig. 3(a). Viewing the structure from the side [Fig. 3(b)], we can see that the spacing between TTF molecules along the stack is 3.57 Å, compared to the much larger 4.54 Å (uniform) spacing between Br^- ions. This results in a Br deficient salt, TTF-$Br_{0.79}$ (3.57 Å/4.54 Å ~0.79). In fact, the TTF molecules and the Br^-

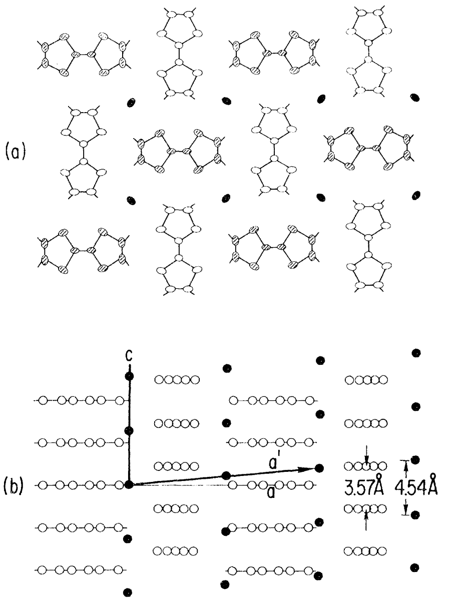

FIG. 3. Crystal structure of TTF-$Br_{0.79}$ as viewed (a) down the c axis (after Ref. 18); and (b) down the b axis (schematic).

ions are found[18] to form two independent, interpenetrating sublattices: the two sublattices have a common stacking direction (c) (but with different, incommensurate dimensions of the unit cell along c), the same b axis, but different a axes [designated[37] a and a' in Fig. 3(b)]. Similar structures have been found for TTF-$I_{0.71}$,[17,21] and TTF-$Cl_{0.79}$,[25] as well as for a number of other recently studied TTF compounds.[19]

Furthermore, La Placa *et al.*[18] found that TTF forms bromide salts with a considerable range of compositions from TTF-$Br_{0.74}$ to TTF-$Br_{0.79}$. Although the x-ray crystal structure was determined only on one crystal with 79% Br, x-ray powder pattern measurements[18] on several samples revealed that as the Br content is decreased, the only major change in the structure is an increase in the Br-Br spacing (which remains uniform). That is, the TTF sublattice remains relatively unchanged and the Br-Br spacing z is related[38] to the Br concentration ρ by $z \simeq 3.57$ Å$/\rho$.

We wish to understand why these salts form with such a large anion-anion spacing along the stack and with an odd stoichiometry.[39] In order to examine if Coulomb interactions can account for these features, we have calculated the classical electrostatic (Madelung) energy for TTF-Br_ρ as a function of ρ; that is, just as TTF-Br_ρ contains a lattice of rigid TTF stacks over the observed range $0.74 \leq \rho \leq 0.79$, with only the Br-Br spacing varying, we consider a series of (hypothetical) TTF-Br_ρ compounds over the entire $0 < \rho \leq 1$ range. Over this extended range, only the Br-Br spacing z is varied and is related to the Br concentration ρ by $z = 3.57$ Å$/\rho$. We will examine the electrostatic (Madelung) energy as a function of Br content or ρ. Such a calculation is of interest since one might guess that the Coulomb repulsion between like charges along the TTF and Br stacks would be large and hence make the formation of the 1:1 compound unfavorable. Indeed, it will be shown that the Madelung repulsion can be significantly reduced if one allows for the formation of the nonstoichiometric salt and that the electrostatic binding energy is the greatest in the vicinity of the observed range of ρ.

Before we can calculate the electrostatic energy of this system, one problem remains: we do not know how the charges are distributed along the mixed-valence TTF stack (average charge of $+\rho$ per TTF molecule) and, therefore, we must find a resonable model for them. As previously stated (and discussed in more detail in Sec. V), we expect the stack to contain neutral (TTF^0) and fully charged (TTF^+) molecules, as opposed to fractionally charged ($TTF^{\rho+}$) molecules.[40] In addition, we would expect that the strong Coulomb repulsion between charged (TTF^+) molecules will keep the charges apart along the stack and the strong Coulomb attraction between these TTF^+ charges and the Br^- ions will concentrate the charge near those TTF molecules which lie closest to the planes containing the bromine ions. Thus, for the Madelung calculation we ignore the neutral TTF molecules and consider a model structure containing *sheets* which have an equal number of Br^- and TTF^+ ions. This model structure also solves a second problem: since the actual TTF and Br sublattices are incommensurate with each other, the lattice sites cannot be generated by translation of a single, electrically neutral primitive cell. This feature would complicate the lattice summation of the Coulomb potentials involved in calculating the Madelung energy. The approximation of neglecting the neutral (TTF^0) molecules simplifies this calculation enormously, particularly for calculating the Madelung energy as a function of the continuous[41] variable ρ.

Although there are a number of such models of the TTF-Br_ρ structure possible, we have chosen the simplest one which contains the essential physics of the effect that we want to describe. (This choice is somewhat arbitrary, but in the region of interest different models are found to give very similar results.) The model, shown schematically in Fig. 4, contains sheets parallel to the $a'b$ plane which have an equal number of Br^- and TTF^+ ions. (The b axis is normal to the plane of Fig. 4). These sheets are separated from adjacent sheets by a variable spacing $z = z_0/\rho$, which is larger than (or equal to, for $\rho = 1$) the spacing $z_0 = 3.57$ Å between neighboring TTF molecules along the stack in TTF-$Br_{0.79}$. The Madelung energy is calculated for a lattice of these sheets, spaced a distance z apart. The dependence on ρ is simulated by varying z. The model is chosen so that for small Br^- concentration (small ρ), the ions form widely separated, quasi-two-dimensional sheets of charge, which would approximately mod-

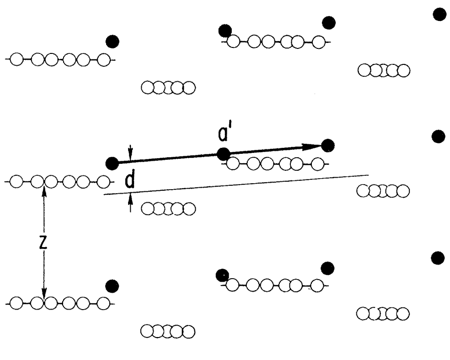

FIG. 4. Model structure of sheets of TTF^+ and Br^- used to approximate the distribution of charges in TTF-Br_ρ for Madelung calculation.

el the expected charge distribution for small ρ (as discussed above). In addition, we have made calculations for the more general case in which the Br^- and TTF^+ ions are each contained in separate, parallel sheets, separated by a (variable) spacing d (Fig. 4).

Although this model structure when viewed normal to the stacking (c) axis (Fig. 4) does not look like the actual structure of $TTF\text{-}Br_{0.79}$ [Fig. 3(b)], the model does look like Fig. 3(a) when viewed down the c axis. We have found that the Madelung energy is relatively sensitive to this distribution of charge normal to the stack and less sensitive to the charge distribution along the stack, e.g., the relative displacements of the Br^- and TTF^+ ions along the stack (as long as $\rho > 0.5$). For the molecular charge distribution over the TTF^+ molecules, we take the CNDO-2 (complete neglect of differential overlap, version 2) charge densities of Metzger and Bloch,[8] listed in Table II. With the use of the Ewald method,[42] we have calculated the Madelung energy $E_M^+(\rho)$ per TTF^+ ion (neglecting the neutral TTF^0 molecules, for the moment) as a function of ρ for several values of d.

The *net electrostatic binding energy* $E_B(\rho)$ normalized per TTF molecule (including both TTF^+ and TTF^0) is given by

$$E_B(\rho) = -\rho\,[\,|E_M^+(\rho)| - (I-A)]\,, \qquad (1)$$

where we include the attractive (negative) Madelung energy E_M^+ per ionized $TTF^+\text{-}Br^-$ pair and the cost $(I-A)$ of ionizing the pair. Using the experimental values[43,44] of $I = 6.85$ eV (obtained in the gas phase) for TTF and $A = 3.56$ eV for Br, we obtain the results shown in Fig. 5. In the low-ρ regime (i.e., large separation between the sheets), the Madelung energy has a definite dependence on the parameter d (which can be simply understood). However, since the results near the minimum are so similar (even for considerably different charge models), we will not spend time describing these differences.

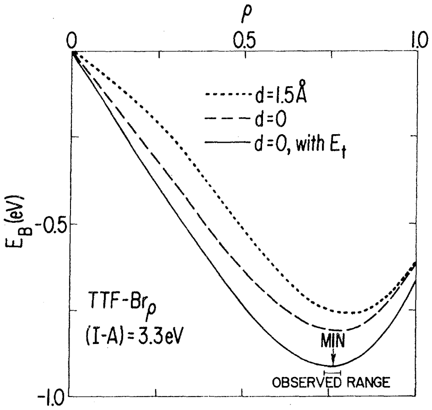

FIG. 5. Results of Madelung calculation for $TTF\text{-}Br_\rho$ showing minimum in net electrostatic binding energy very near observed composition range.

TABLE II. Fractional atomic charges for TTF^+ and $TCNQ^-$, after Metzger and Bloch (Ref. 8). Atom labels as in Ref. 59.

TTF^+		$TCNQ^-$	
S1	0.1103	C4	0.1569
S2	0.1161	C5	0.1573
C1	0.0292	C6	−0.1303
C2	0.0263	C7	0.0541
C3	0.0448	C8	−0.0281
H1	0.0868	C9	−0.0253
H2	0.0865	N1	−0.3152
		N2	−0.3201
		H8	−0.0235
		H9	−0.0258

The general, physical interpretation of the results in Fig. 5 is independent of the structural model: as Br^- is added and ρ increases, the binding energy per TTF molecule (including neutrals) initially increases as the percentage of ionized TTF^+ molecules increases; but as ρ approaches[45] 1 and $Br^-\text{-}Br^-$ spacing gets shorter, the repulsion starts to dominate, giving rise to a minimum in the electrostatic binding energy as a function of ρ.

In addition to the electrostatic energy, we can also investigate the band energy $E_t(\rho)$ associated with electronic delocalization along the stacks, which we have heretofore explicitly and implicitly assumed to be small compared to the Coulomb interactions. It is difficult to estimate this energy if such strong Coulomb interactions are also present. We know only of the calculations by Shiba[46] for the limiting case of the Hubbard model,[2] where only the on-site (intramolecular) Coulomb repulsion U is considered. Shiba has calculated[46] the zero-temperature ground-state energy E_t of a one-dimensional stack, shown in Fig. 6 as a function of the number of electrons per site ρ. The electrons have a transfer integral t (bandwidth $4t$) and an on-site Coulomb repulsion energy U. For $U = 0$, the minimum in the energy is seen to correspond to one electron per site (half-filled). In general, however, $U \neq 0$ and, in fact, U is probably quite large (~1 eV) in these systems.[2,14,25-27,47] In this case, Fig. 6 shows that the energy favors $\rho < 1$ and in the limit $U \gg t$, the minimum is at $\rho = 0.5$. For most charge-transfer salts, however, the magnitude of this contribution is relatively small, since t is expected to be less than 0.15 eV.[1,2] Nevertheless, it could well be the dominant attractive force along the chain and essential for stabil-

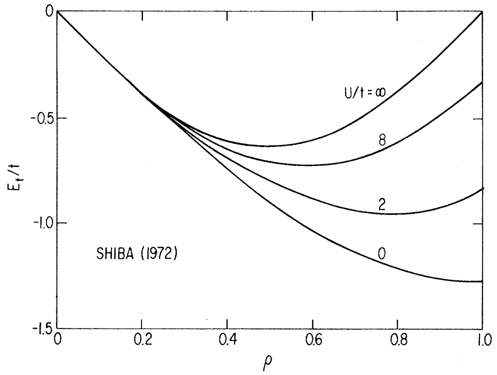

FIG. 6. Ground-state energy of the Hubbard model for various values of U/t (after Shiba), which is used as a measure of the band energy gained by delocalizing the electrons along the stack.

izing the close TTF-TTF spacing of 3.57 Å (see Sec. IV). Using values of $t = 0.15$ eV and $U = 1.2$ eV, we calculate E_t and add it to the net Madelung binding energy $E_B(\rho)$ (for $d = 0$) in Fig. 5. The inclusion of the kinetic energy is seen to make a small, but important, contribution to the location of the minimum.

The values of ρ in the region of this broad minimum are in remarkably good agreement with the observed[18] range: $0.74 \leqslant \rho \leqslant 0.79$. The value of ρ thus calculated from the minimum in Fig. 5 is relatively insensitive, not only to the different model structures used, but also to the charge distribution within the TTF$^+$ molecule and the values of t and U used in calculating E_t. On the other hand, a different value of $I - A$ (if it were appropriate) would have a somewhat larger effect on the value of ρ at the minimum: for example, a value of $I - A$ which is 0.2 eV smaller than that used in Fig. 5 would shift the minimum from $\bar{\rho}$ $\cong 0.78$. At the same time the binding energy at the minimum would be increased from 0.91 to 1.06 eV. In this case, the agreement with experiment would still be remarkably good.

We now consider extending these results to the chloride[48] and iodide salts of TTF. Since these structures[17,21,25] very closely resemble that[18] of the bromide salt, we assume that the most important difference is in the values of the halide electron affinities. As summarized on Table II, the electron affinities[44] are ~0.22 eV higher for Cl and ~0.28 eV lower for I, compared with Br. Using these new values for $(I - A)$ (Table III), we calculate the optimum ρ to be $\bar{\rho} \cong 0.78$ for TTF-Cl$_\rho$ and $\bar{\rho} \cong 0.70$ for TTF-I$_\rho$, compared to the respective experimental values of ~0.79 and ~0.71 (Table III). (Both of these experimental values may not be exactly in the middle of their composition range.)

TABLE III. Comparison of calculated and observed compositions of various halide salts of TTF and TSeF.

	$I - A$ (eV)	$\bar{\rho}_{\rm calc}$	$\bar{\rho}_{\rm expt}$	
TTF-Cl$_\rho$	3.07	0.78	~0.79	(Ref. 25)
TTF-Br$_\rho$	3.29	0.74	0.74–0.79	(Ref. 18)
TTF-I$_\rho$	3.57	0.70	0.71	(Refs. 17, 21)
TSeF-Br$_\rho$	~3.49	~0.78	~0.80–0.86	(Ref. 25)

For the bromide salt of tetraselenafulvalene (TSeF) (where the four sulfurs have been replaced by seleniums[49]), a separate Madelung calculation is needed because of the different molecular charge density of TSeF, even though its structure[25] resembles that of TTF-Br$_{0.79}$. If we neglect the differences in charge density, it is instructive to use the results from the TTF-Br$_\rho$ calculation. Two separate effects must be taken into account: (i) the ~0.20-eV increase[50] in the ionization potential I of TSeF would cause a ~0.04 decrease in ρ; but (ii) the ~10% increase in lattice spacing along the stack (expected due to the increased van der Waals radius of Se) would cause a 10% increase in z_0 and hence a ~0.08 increase in ρ. The estimated *net* increase of ~0.04 in ρ to ~0.78 should be compared with the preliminary values[26] of ρ ~ 0.80–0.86 for TSeF-Br$_\rho$.

It should be recognized that some other possibly important interactions have not been included (see Sec. III). The good agreement obtained using *only* classical electrostatic interactions suggests that these interactions are the most important for determining ρ, at least in the case of the TTF-Br$_\rho$ system. Perhaps a more sensitive indication of the value of this calculation is the good agreement with the trends in the other halide salts (Table III). Thus, TTF-Br$_\rho$ with $\rho = 1$ would be too repulsive and the electrostatic binding is enhanced for a mixed valence, partly ionic stack of TTF molecules, with the Br$^-$ ions uniformly spaced at ~4.54 Å apart. We strongly emphasize that the present calculation of this minimum in electrostatic energy (Fig. 5) does not represent a calculation of lattice *stability* (see Sec. IV).

Let us now turn to the charge-transfer salts of TCNQ. Of the ~250 known TCNQ charge-transfer salts with segregated stacks, ~70% form complex salts for a very wide variety of donors, e.g., TEA-TCNQ$_2$ [Fig. 2(c)] (TEA, triethylammonium). We suggest that so many such salts are formed for the same reason that TTF-Br$_\rho$ forms with $\rho < 1$, i.e., in order to reduce the repulsion between charges along the stack. In the case of TTF-Br$_\rho$, the small, spherical Br^- ions can easily fit into the channels between the TTF columns, with any spacing—hence we can consider ρ as a continuous[41] variable. But for the odd-shaped donor molecules in the complex TCNQ salts, steric factors favor 1:2, 2:3, or 1:1 salts.

As a logical extension of this work, we suggest that the odd stoichiometry found in the Krogmann salts,[51] e.g., $K_2Pt(CN)_4Br_{0.30} \cdot 3H_2O$, could have the same physical origin as TTF-Br_ρ. This suggestion has been independently made recently by Messmer and Salahub.[52]

III. SIMPLE SALTS AND INCOMPLETE CHARGE TRANSFER

In Sec. II, it was shown how the Coulomb repulsion between charges along the stack was reduced in the case of TTF-$Br_{0.79}$ by forming a salt with a deviation from a 1:1 donor to acceptor ratio. In simple TCNQ salts, where there is an equal number of donors and acceptors, is there another way possible in which this repulsion could be decreased? We suggest[10] that the Coulomb repulsion along the stack can, in some cases, be appreciably decreased by incomplete transfer of charge from donor to TCNQ, leaving an average of ρ electrons per TCNQ molecule ($\rho < 1$). (Very recently this suggestion has been independently made by Klymenko *et al.*[11] for TTF-TCNQ.) In the resulting crystal of neutral and charged molecules, the charged molecules might be expected to form sheets of donor and TCNQ ions (as discussed earlier). Neglecting the neutral molecules, we could approximate this structure by sheets of charge separated by a spacing $z = z_0/\rho$, where z_0 is the spacing between molecules along the stack. This model structure is identical (since we have neglected the neutral molecules) to the original structure, but with an increased spacing z along the stack. Using this as our model of the charge distribution in the crystal, we can calculate the net electrostatic binding energy as a function of the degree of charge transfer ρ using Eq. (1).

For Na-TCNQ and the two phases of Rb-TCNQ Metzger[6] has calculated the net electrostatic binding energy [E_B^F (Table I)] for $\rho = 1$, i.e., for complete transfer of charge from donor to TCNQ. Similar results were obtained for Rb-TCNQ (I) by Vegter and Kommandeur.[7] (For completeness, we have also included results[53] for tetramethyl-*p*-phenylenediamine-iodide (TMPD-I) in Table I.) In these examples the net binding energy is ~3 eV per molecule, as expected for a strongly bound ionic crystal. For $\rho = \frac{1}{2}$ (and hence $z = 2z_0$), Metzger[54] has kindly calculated for us the binding energy for Rb-TCNQ (I). This value is used with the $\rho = 1$ value to estimate $E_B(\rho)$ for Rb-TCNQ (I) in Fig. 7. This energy curve if extended for $\rho > 1$ would eventually have a minimum for some larger value of ρ. But since ρ is restricted[45] to be less than 1, the lowest energy is at $\rho = 1$, as it is for Na-TCNQ and Rb-TCNQ (II), presumably. Thus, the Madelung energy favors *complete* charge transfer for these salts, in agreement with what is concluded[13,1] based on their physical properties.

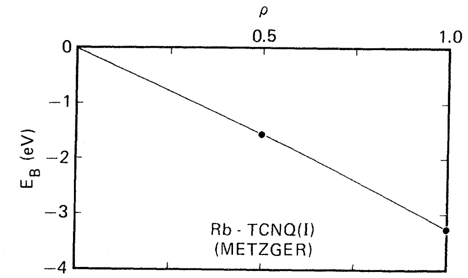

FIG. 7. Net electrostatic binding energy calculated for Rb-TCNQ(I).

In the case of TTF-TCNQ, we have made a similar calculation of the net binding energy as a function of charge transfer (ρ). Using the expected value[6,43,55] of $I - A = 4.05$ eV and neglecting the small contribution of E_t, we show in Fig. 8 the calculated[56] values of $E_B(\rho)$ per TTF-TCNQ molecular pair, Eq. (1), by the ×'s where we regard ρ as a continuous variable. Recently, Metzger and Bloch[8] (at our suggestion) performed a similar calculation at $\rho = \frac{1}{2}$, but included the interactions

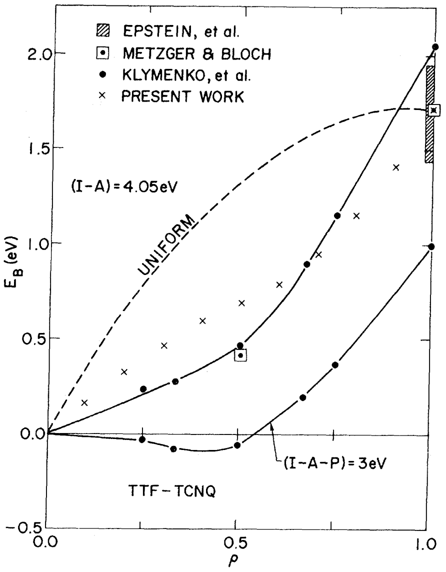

FIG. 8. Results (×) of Madelung calculation for TTF-TCNQ, neglecting neutral molecules. Results of Refs. 8–11 are also included and discussed in text.

with the neutral TTF^0 and $TCNQ^0$ molecules. This result is shown by the open square in Fig. 8 along with their result for $\rho = 1$ (full charge transfer). [Their results assuming a uniform charge distribution but variable ρ (dashed lines in Fig. 8) are discussed in Sec. V.] For $\rho = 1$, both their and our calculations are equivalent and give exactly the same result. For $\rho = \frac{1}{2}$ their model of the structure contains sheets of charged molecules alternating with sheets of neutral molecules, while our calculation neglects the neutral molecules. Comparing the two results in Fig. 8, the effect of the neutral sheets is to lower the Madelung energy by ~15%, and the net binding energy by ~0.2 eV. Thus, the neutrals play a significant role in determining the exact energies. This effect is not too surprising when one realizes that, although the net charge on the neutral molecules is zero, there are large negative charges[8] on the CN groups in $TCNQ^0$, for example. In contrast, the quadrupole moment in TTF^0 is much smaller[8,9] and the effects of neglecting TTF^0 in the TTF-Br_ρ calculations (Sec. II) are not nearly so serious as neglecting $TCNQ^0$ in TTF-TCNQ. (More recently we have included the neutral TTF^0 and $TCNQ^0$ molecules for $\rho = \frac{1}{2}$ and have reproduced the result of Metzger and Bloch.[8])

Very recently Klymenko *et al.*[11] have independently suggested some of the ideas presented in this paper. In particular, they carried out similar calculations, including neutral molecules, for $\rho = \frac{1}{4}, \frac{1}{3}, \frac{1}{2}, \frac{2}{3}, \frac{3}{4}$, and 1, which are shown by the solid points in Fig. 8. Since this group used a different molecular charge density, the lack of agreement with Metzger and Bloch for $\rho = 1$ and $\rho = \frac{1}{2}$ indicates the (weak) sensitivity of the net binding energy to choice of molecular charge densities. For other sets of charge densities, Epstein *et al.*[9] have calculated the Madelung energy for $\rho = 1$, with similar results (Fig. 8). The general trend of all the results is quite similar, although somewhat dependent on how the structure is modeled (e.g., whether or not neutrals are included) and which charge density is used.

For NMP-TCNQ, only calculations for $\rho = 1$ have been made. Metzger[12] found that the net electrostatic binding energy is ~+3.7 eV (repulsive), using the recently obtained value[57] of $I - A = 3.7$ eV.

It is clear from Table I and from a comparison of Figs. 7 and 8 that the alkali-TCNQ salts are much more strongly bound by electrostatic interactions than TTF- and NMP-TCNQ. For example, for $\rho = 1$ the net binding energies calculated for Na-TCNQ (−3.0 eV) and for the two phases of Rb-TCNQ (−3.3 and −3.2 eV) are much more binding than those calculated for TTF-TCNQ (+1.7 eV) and NMP-TCNQ (+3.7 eV). We suggest that there are two principle reasons for this large difference in the calculated binding energy: (i) the ionization energies of TTF and NMP are estimated[43,57] to be from ~1.5 to 2.5 eV higher than those[58] of the alkali donors (Table I); and (ii) the intrasheet binding (the attractive part of the electrostatic energy) is considerably weaker in TTF and NMP-TCNQ. A simple quantity related to the strength of the intrasheet (or interstack) binding energy is the number of chains per unit area. For[59] TTF-TCNQ and[60] NMP-TCNQ this quantity is seen to be only ~60% as large as for the alkali salts,[61-63] NH_4-TCNQ,[64] and[65] morpholinium-TCNQ (Table I). This indicates that there is a weaker intrasheet attraction for salts with donor molecules that are as *large in size* as TTF and NMP. In fact, an actual calculation of the intrasheet binding energy gives 2.4 eV for TTF-TCNQ, compared to the value[54] of 4.9 eV for Rb-TCNQ. Thus, we believe that these are the two primary factors responsible for the result that $|E_M^F| < I - A$ for TTF- and NMP-TCNQ (as fully-charged transferred salts).

One of the major features of the TTF-TCNQ results of Fig. 8 has been pointed out by each of the groups[8-11]: the simple rule of thumb implies that TTF-TCNQ is unstable for $\rho = 1$; i.e., the Madelung energy gained [−(1.8–2.3) eV] is less in absolute value than the estimated cost of ionizing the lattice, $I - A = 4.05$ eV. The major emphasis of Metzger and Bloch[8] and Epstein *et al.*[9] is to discuss other interactions which contribute to the crystal binding. A common conclusion is that the metallic binding is very small, but that the "polarization energy" may play an important role. Recent attempts to calculate this energy, however, by Klymenko *et al.*,[11] Bush,[66] Metzger,[67] as well as Silverman, Grobman, and Torrance[68] have yielded only a small energy. For example, Silverman *et al.*[68] find that the dipolar polarization energy for $\rho = 1$ contributes only ~0.09 eV to the crystal binding of TTF-TCNQ.

Klymenko *et al.*[11] use a value of $I - A = 3$ eV, compared with the more widely accepted value of $I - A = 4.05$ eV. The choice of such a low value could represent the effective reduction of $I - A$ by polarization effects, but this choice is unjustified without a calculation confirming such a large polarization energy. For comparison, their data using this smaller value of $I - A$ are also shown in Fig. 8. It is seen that in this case the energy becomes very weakly binding near $\rho \sim 0.3$. To summarize, the crystal binding in TTF-TCNQ cannot be adequately described by electrostatic interactions alone (as was possible for TTF-Br_ρ) and it is not yet clear which additional energies are responsible for binding the crystal.

The original goal of this work was not (and is not) to determine why $\rho > 0$, i.e., why there is any charge transfer at all. Rather, we wanted to show how the electrostatic energy favors $\rho < 1$, i.e., incomplete charge transfer, since it was initially believed that the charge transfer was complete.[69] Although other interactions are undoubtedly important in TTF-TCNQ (e.g., polarization energy), it is clear from Fig. 8 that a Wigner-crystal-like charge distribution with $\rho \sim 0.5$ has ~1 eV per molecule more electrostatic binding energy than the fully charge transferred ($\rho = 1$) state. We therefore suggest that this is a very important factor, if not the most important factor, which makes incomplete charge transfer energetically favorable. The repulsion between charges along the stack is reduced by effectively increasing the separation between them with incomplete charge transfer.

Indeed, experimental evidence for incomplete charge transfer in TTF-TCNQ has come from x-ray photoemission[28] and optical[14] measurements. Quantitative and more convincing evidence has very recently come from both diffuse x-ray[70,71] and neutron scattering[72,73] results, which indicate[27] that $\rho = 0.59$.

These same Madelung energy considerations suggest that NMP-TCNQ is also characterized by incomplete charge transfer. Although no diffuse x-ray or neutron measurements have yet been performed on this salt, there is strong evidence for incomplete charge transfer from magnetic susceptibility,[74,75] optical,[14] NMR,[76] thermopower,[77] and[78] EPR measurements.

IV. STABILITY OF IONIC GROUND STATES

In order to determine (theoretically) whether the ground state in a molecular solid is ionic or nonionic, McConnell, Hoffman, and Metzger[4] have suggested a simple criterion: if the Madelung energy E_M gained by forming the crystalline ionic structure is larger than the cost $(I - A)$ of ionizing the molecules, then the ground state will be ionic. Otherwise, it will be nonionic. In other words the energy per donor-acceptor pair should be lower for the charge-transferred, ionized crystal than for the crystal composed of neutral molecules. This simple rule of thumb has been used in connection with all of the Madelung calculations[5-11] on TCNQ salts (even if used only as a point of departure to suggest that other contributions to the energy must be considered to provide the existence of an ionic ground state).

It should be clearly recognized, however, that this simple, useful, rule of thumb says nothing about the lattice *stability* of an ionic ground state. For example, Earnshaw's theorem states[79] that a classical system of point charges under the interaction of Coulomb forces alone cannot be stabilized. In fact, the Coulomb repulsion (if that were all that was present) between molecules along the stack would make the crystal blow up along the stacking direction. The lattice must be bound along each direction, i.e., the square of the frequencies of all the normal vibrational modes of the crystal must be real and positive. It should therefore be emphasized that the condition $|E_m| > I - A$ is neither a necessary nor a sufficient condition for the lattice stability of an ionic ground state. It is not a necessary condition since other contributions to the binding energy as well as the Madelung energy are important. It is not a sufficient condition since the ions must be at potential minima for the lattice to be stable. Therefore, if a given calculation yields $|E_m| > I - A$, one can only conjecture concerning the crystal stability. In this context, the minimum in the energy versus ρ for TTF-Br_ρ in Fig. 5, for example, indicates that a structure with $\rho \sim 0.74$ has a larger electrostatic binding energy than for any other value of ρ. It represents a comparison of the energies of different charge configurations in order to see which has the minimum energy. Such states with minimum energy are clearly energetically favored and are undoubtedly more easily stabilized.

The brief discussion in this section of the relationship between stability and binding energy is nicely illustrated by the following example. Let us consider very qualitatively the stability of the lattice of a salt similar to Rb-TCNQ (I) *along the*

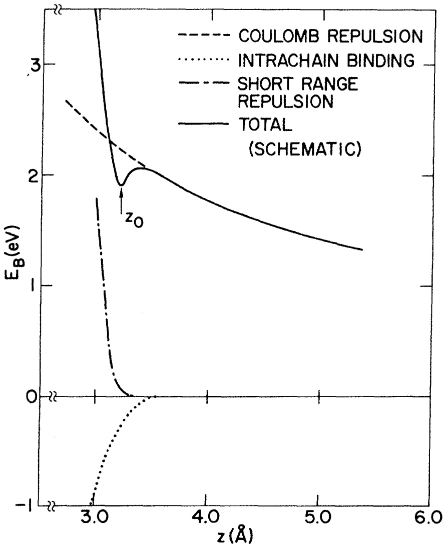

FIG. 9. *Schematic* of three contributions which affect the stability along the stacking axis of a salt like (Rb-TCNQ(I).

stacking direction. For illustrative purposes, we include only three interactions: (i) the large Coulomb repulsion between electrons along the stack[9] (~2 eV for $z \sim 3.2$ Å); (ii) the short-range attraction (~0.2 eV) due to the transfer integral (band energy); and (iii) the short-range repulsion. As indicated schematically in Fig. 9, the magnitude of the energy is still dominated by the Coulomb repulsion along the stack. Nevertheless, the other interactions might give rise to a local minimum in the net binding energy, making the crystal *stable* to changes of the molecular separation along the stacking axis. In order to determine whether the crystal is *binding* at this minimum, we must also include all other contributions to the energy, e.g., the attractive interstack contribution.

V. MODULATED CHARGE DENSITY—CDW

The simple description of the general features of electrostatic binding in these and related materials which was given by McConnell, Hoffman, and Metzger[4] also contains some conclusions about the degree of charge transfer ρ. For an alternating stack or a uniform distribution of ρ electrons per site along a segregated stack, the Madelung energy $E_M(\rho)$ is proportional[80] to ρ^2, while the cost of transferring a fractional charge ρ from donor to acceptor is linear[81] in ρ. So that

$$E_B(\rho) = -\rho\left[\,|E_M^F|\,\rho - (I-A)\right], \tag{2}$$

where E_M^F is the Madelung energy (assumed attractive) for full charge transfer ($\rho = 1$). In Fig. 10, $E_B(\rho)/|E_M^F|$ is plotted for several values of $(I-A)/|E_M^F|$. If $(I-A) > |E_M^F|$, $E_B(\rho)$ has its lowest energy for $\rho = 0$ (no charge transfer), while if $(I-A) < |E_M^F|$, the lowest energy is at $\rho = 1$ (full charge transfer). This result is the simple rule of thumb discussed earlier, but with one additional conclusion: for an alternating stack,[4] the ground state has *either* $\rho = 0$ or $\rho = 1$, but never partial or incomplete charge transfer.[82] The same conclusion holds for a segregated stack if the charge distribution is uniform. Other interactions, for example, the polarization energy, as long as they vary as ρ^2 or as ρ (as might be expected), would not alter the above conclusion. However, their exact dependence on ρ is uncertain.[9]

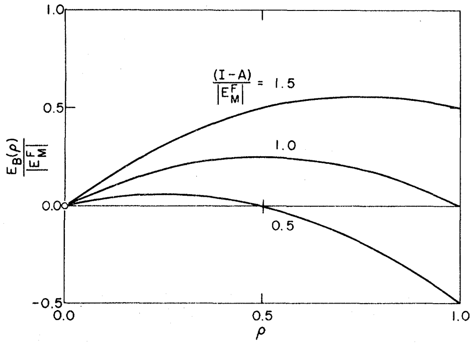

FIG. 10. Plot of Eq. (2) as a function of ρ showing that the lowest energy occurs at *either* $\rho = 0$ or $\rho = 1$.

Equation (2) and the conclusions derived from it are valid only if the average charge ρ per molecule is *delocalized* down the chain and is distributed *uniformly* over equivalent sites. One of the most important points of the present paper is that in some cases one should consider the possibility that the charge is partially *localized* and varies from site to site down the stack, forming a *modulated* charge density, or charge-density wave (CDW). Such a case is a crystal such as that shown in Fig. 1, where there are attractive interactions in some directions and repulsive interactions in other directions. When the charge ρ is decreased from $\rho = 1$ *uniformly* along the stack, the repulsive and attractive contributions decrease at the same rate (~ρ^2), Eq. (2). In a crystal such as Fig. 1, however, it is possible to decrease ρ in such a way that the repulsive part decreases considerably faster than the attractive part. In the example suggested in this paper, the repulsion along the stack is decreased much faster than the intrasheet attractive contribution. This is accomplished by increasing the average separation between charges along the stack by having neutrally charged molecules in between the charged ones, and hence making a highly modulated distribution of localized charges along the stack.

For TTF-TCNQ it is possible to compare the results of calculations using such strongly modulated charged distribution (×'s and solid points in Fig. 8) with that for the uniform case calculated by Metzger and Bloch[8] (dashed curve in Fig. 8). Clearly there is a very significant gain in binding energy by modulating the distribution of localized charges. For $\rho = 0.5$, for example, the modulated charge distribution (including the neutral molecules) gives *more than twice* the Madelung binding of the uniform distribution.

In this context, the conclusion of Sec. III must be broadened to include the close relation between incomplete charge transfer and modulated charge distribution: *a significant increase in the electrostatic binding energy can be gained in TTF-TCNQ by having incomplete charge transfer, but only if the charge distribution is modulated.* Correspondingly, *a ground state with incomplete charge transfer implies a modulated charge distribution* *with partially localized charges.*

We now consider just how modulated we can expect the charge distribution to be. If we could completely neglect the band energy of the electrons along the stack, the charges would be completely localized and the charge distribution down the stack would be the most modulated possible: with molecules charged either 0 or 1 (and not fractionally). The charged molecules would then form sheets of charge, making what could be called a Wigner crystal.[31] This extreme case is the one that we have considered (partially for calculational ease) in order to illustrate the points and conclusions we wanted to draw. Since the transfer integral for electrons down the chain is estimated[1,2] to be ~0.1 eV, while the relevant Coulomb interactions[9] are of order 1–2 eV, the neglect of t is a very good approximation. Although the exact ground state of a set of charges with strong Coulomb interactions and weak band energy is not known, we can reason[27] some of the qualitative features: the effect of the transfer integral would be to delocalize the charges along the stack. This delocalization would undoubtedly tend to decrease the amplitude of modulation of the charge distribution compared to the extreme case considered in this paper. However, the charges would tend to delocalize in a correlated way, so as to maintain the distribution as modulated as possible. This modulated charge distribution, or charge-density wave (CDW), would be incommensurate and dynamic, rather than static. Thus, the CDW in a real crystal would not be as modulated as in the extreme case which we have used for our calculations. Nevertheless, there will be considerable modulation (i.e., the amplitude of the CDW will be large) and all of the general conclusions of this paper will remain qualitatively valid.

Recently, diffuse x-ray scattering at "$4k_F$" has been discovered[32,33] in TTF-TCNQ which is present at room temperature. In addition, x-ray measurements[18,21] have uncovered a modulation along the stack of the positions of the TTF molecules in TTF-$Br_{0.79}$ and TTF-$I_{0.71}$. We interpret[27,34] these effects as indicating the existence of *CDW's, that are caused largely by the strong Coulomb interactions* (as described above) and are observed through their effect on the phonons.

Equation (2) has also been discussed recently by Merrifield,[83] who added the dependence on temperature, i.e., the charge transfer is determined, not by the energy, but by the free energy. The additional entropy term is proportional to the temperature and favors $\rho = \frac{2}{3}$ (incomplete charge transfer). As the temperature is raised, the magnitude of this term increases (linearly), thus tending more to favor $\rho = \frac{2}{3}$. In this way this term gives rise to a temperature-dependent ρ, which in some special cases may change discontinuously, causing a phase transition. In practice, the magnitude of this term is ~kT and since this value (~$\frac{1}{40}$ eV) at room temperature is much smaller than the other terms (1–5 eV), it can safely be neglected in most cases. For example, using the data of Fig. 8, the temperature of the predicted discontinuity in ρ in TTF-TCNQ would occur near 10 000 °K. This work has recently been extended by Chang, Jafarey, and Scalapino[84] to include effects of finite bandwidth, with and without correlation.

VI. CONCLUSION: RELATION BETWEEN MADELUNG ENERGY AND CHARGE TRANSFER

The principal conclusions of this paper can be summarized by examining Fig. 11. Here we have included the results for the net electrostatic binding energy $E_B(\rho)$ for TTF-Br_ρ, Rb-TCNQ(I), and TTF-TCNQ as a function of ρ, the average number of electrons per organic molecule. The large difference in binding energy between Rb-TCNQ(I) and TTF-TCNQ has been attributed to two factors: (i) the larger ionization potential[43] of TTF (6.85 eV) compared to that[58] of Rb (4.2 eV); and (ii) the

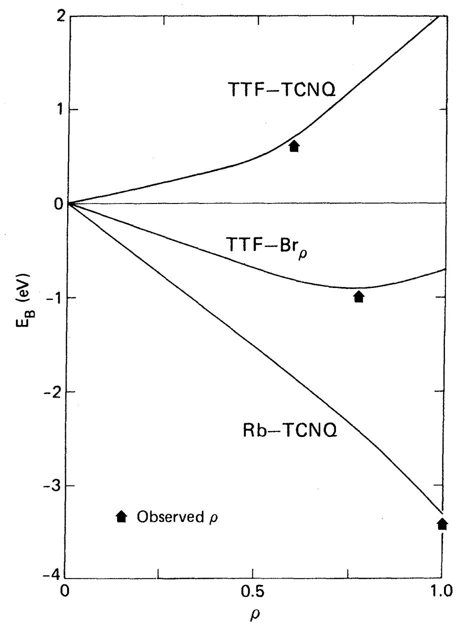

FIG. 11. Net electrostatic binding energy calculated for TTF-Br_ρ, Rb-TCNQ(I), and TTF-TCNQ, illustrating the relationship between this energy and the observed value of the charge transfer (given by the arrows). Data of Ref. 11 are used for the TTF-TCNQ curve.

weaker *interstack* electrostatic binding (related partially to the larger size of the TTF molecule). In fact, the initial slope of the curves in Fig. 11 is equal to the sum of $(I-A)$ and the Madelung energy per sheet (see Sec. III). For Rb-TCNQ (I) these contributions are each 2.5 eV larger, than for TTF-TCNQ, accounting for the steep downward slope of the Rb-TCNQ(I) curve in Fig. 11. Also shown in this figure by the arrows are the experimentally observed values of ρ.

Although a large number of contributing factors undoubtedly determine ρ, the data in Fig. 11 indicate that the electrostatic energy is one of the most important. The general feature of Fig. 11 is unmistakable: *materials with weaker net electrostatic binding energy have lower values of* ρ. Physically, if the overall Madelung binding is weak and/or $I-A$ is large, the repulsion between like charges along the stack must be decreased. It is reduced by decreasing ρ and forming a nonuniform charge distribution along the stack (CDW), which increases the average separation between charges along the stack. This is a characteristic feature of charge transfer salts with segregated stacks and is one of the most important factors for governing[13,14] the wide variety of electrical and magnetic properties found in these materials; for example, the factor of 10^6 between the room-temperature conductivities of Rb-TCNQ (I) and TTF-TCNQ.

Note added in proof: A recent paper by I. I. Ukrainskii, V. E. Klymenko, and A. A. Ovehinnikov (unpublished) extends their earlier work (Ref. 11). Specifically, they calculate a value of $E_M^F = -2.4$ eV for NMP-TCNQ, in contrast to the value of ~0 (Table I) obtained in Ref. 12.

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[1] I. F. Shchegolev, Phys. Status Solidi A 12, 9 (1972).

[2] Z. G. Soos, Ann. Rev. Phys. Chem. 25, 121 (1974).

[3] Y. Tomkiewicz, J. B. Torrance, B. A. Scott, and D. C. Green, J. Chem. Phys. 60, 5111 (1974).

[4] H. M. McConnell, B. M. Hoffman, and R. M. Metzger, Proc. Natl. Acad. Sci. USA 53, 46 (1965).

[5] R. M. Metzger, J. Chem. Phys. 57, 1870 (1972).

[6] R. M. Metzger, J. Chem. Phys. 63, 5090 (1975).

[7] J. G. Vegter and J. Kommandeur (unpublished). They use a different molecular charge distribution than Ref. 6.

[8] R. M. Metzger and A. N. Bloch, Bull. Am. Phys. Soc. 20, 415 (1975); J. Chem. Phys. 63 5098 (1975).

[9] A. J. Epstein, N. O. Lipari, D. J. Sandman, and P. Nielson, Bull. Am. Phys. Soc. 20, 465 (1975); Phys. Rev. B 13, 1569 (1976).

[10] J. B. Torrance and B. D. Silverman, Bull. Am. Phys. Soc. 20, 498 (1975).

[11] V. E. Klymenko, V. Ya. Krivnov, A. A. Ovchinnikov, I. I. Ukrainsky, and A. F. Shvets, Zh. Eksp. Teor. Fiz. 69, 240 (1975) [Sov. Phys.-JETP 42, 123 (1976)].

[12] R. M. Metzger, J. Chem. Phys. 57, 2218 (1972).

[13] J. B. Torrance (unpublished).

[14] J. B. Torrance, B. A. Scott, and F. B. Kaufman, Solid State Commun. 17, 1369 (1975).

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

[16] E. A. Perez-Albuerne, H. Johnson, Jr., and D. J. Trevoy, J. Chem. Phys. 55, 1547 (1971).

[17] J. J. Daly and F. Sanz, Acta. Crystallogr. B 31, 620 (1975).

[18] S. J. LaPlaca, P. W. R. Corfield, R. Thomas, and B. A. Scott, Solid State Commun. 17, 635 (1975).

[19] F. Wudl, J. Am. Chem. Soc. 97, 1962 (1975); and F. Wudl *et al.* (unpublished).

[20] G. R. Johnson, D. J. Dahm, M. G. Miles, and J. D. Wilson, Bull. Am. Phys. Soc. 20, 466 (1975).

[21] C. K. Johnson and C. R. Watson, Jr., J. Chem. Phys. 64, 2271 (1976).

[22] R. J. Warmack, T. A. Callcott, and C. R. Watson, Phys. Rev. B 12, 3336 (1975).

[23] R. B. Somoano, A. Gupta, V. Hadek, T. Datta, M. Jones, R. Deck, and A. M. Hermann, J. Chem. Phys. 63, 4970 (1975).

[24] D. J. Dahm, G. R. Johnson, F. L. May, M. G. Miles, and J. D. Wilson, Cryst. Struct. Commun. 4, 673 (1975).

[25] B. A. Scott, S. J. LaPlaca, J. B. Torrance, B. D. Silverman, and B. Welber (unpublished).

[26] B. A. Scott, J. B. Torrance, S. J. LaPlaca, P. W. R. Corfield, D. C. Green, and S. Etemad, Bull. Am. Phys. Soc. 20, 496 (1975); and unpublished results.

[27] J. B. Torrance, Proceedings of Nato Advanced Study Institute on *Chemistry and Physics of One-Dimensional Metals*, Bolzano, edited by H. J. Keller (Plenum, New York, in press).

[28] W. D. Grobman, R. A. Pollak, D. E. Eastman, E. T. Maas, Jr., and B. A. Scott, Phys. Rev. Lett. 32, 534 (1974); S. F. Lin, W. E. Spicer, and B. H. Schechtman, Phys. Rev. B 12, 4184 (1975); W. D. Grobman and

B. D. Silverman, Solid State Commun. 19, 319 (1976).

[29] A. J. Epstein, N. O. Lipari, P. Nielson, and D. J. Sandman, Phys. Rev. Lett. 34, 914 (1975).

[30] J. J. Ritsko, N. O. Lipari, P. C. Gibbons, and S. E. Schnatterly, Bull. Am. Phys. Soc. 21, 311 (1976).

[31] E. Wigner, Trans. Faraday Soc. 34, 678 (1938).

[32] J. P. Pouget, S. K. Khanna, F. Denoyer, R. Comès, A. F. Garito, and A. J. Heeger, Phys. Rev. Lett. 37, 437 (1976).

[33] S. Kagoshima, T. Ishiguro, and H. Anzai (unpublished).

[34] J. B. Torrance, H. A. Mook, and C. R. Watson (unpublished).

[35] V. J. Emery, Phys. Rev. Lett. 37, 107 (1976).

[36] R. P. Shibaeva and L. O. Atomyan, J. Struct. Chem. 13, 514 (1972).

[37] The authors of Ref. 18 have chosen another (completely equivalent) Br sublattice with $\beta' = 116.01°$ and $a' = 17.368$.

[38] There is a systematic difference (Ref. 18) between the values of ρ obtained from chemical analysis and those from x-ray measurements (the latter are 0.05 higher). We use the x-ray results since we are interested in the Br-Br-spacing. (See also Ref. 25).

[39] Since the halide-halide spacing should be greater than twice their van der Waal radii, ρ should be less than 0.99, 0.92, and 0.83 for TTF-Cl_ρ, TTF-Br_ρ, and TTF-I_ρ, respectively. The fact that the observed (uniform) halide-halide spacings are considerably larger (ρ smaller) (see Table III) than these values insures that the observed values of ρ are not determined by these radii. This fact also indicates that the halide ions do not interact with each other and that they are fully charged.

[40] A calculation using fractional charges on the *TTF-molecules* would have the same qualitative features for TTF-Br_ρ as we find for our model. As discussed in Sec. V, these features are associated with a modulated charge density and will remain if the TTF stack is made uniform, since the charge density on the Br stack is still modulated.

[41] Commensurate values of ρ do not appear to be important in the TTF halide systems. In the Br system, the observed range of ρ includes $\frac{3}{4}$ and comes close to $\frac{4}{5}$, but nothing special occurs at these values. In addition, the observed TTF : I composition ratio is 5.023 : 7 and definitely not 5 : 7 (Ref. 21).

[42] M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford U. P., London, 1954).

[43] R. Gleiter, E. Schmidt, D. O. Cowan, and J. P. Ferraris, J. Electron. Spectrosc. 2, 207 (1973).

[44] L. Pauling, *The Nature of the Chemical Bond* (Cornell U. P., Ithaca, N. Y., 1960), p. 511.

[45] To go beyond $\rho = 1$ would cost $I_2 - A_2$ (the second ionization potential minus the second electron affinity). Since this is such a large energy, we restrict ourselves to $\rho \leq 1$.

[46] H. Shiba, Phys. Rev. B 6, 930 (1972).

[47] J. B. Torrance, B. A. Scott, B. Welber, and F. B. Kaufman (unpublished).

[48] Here we discuss the *ordered* phases of TTF-Br_ρ and TTF-Cl_ρ with $\rho \sim 0.76$ and 0.79, respectively. The *disordered* phases with $\rho \sim 0.57$ and 0.68, respectively, are more fully discussed in Ref. 25.

[49] E. M. Engler and V. V. Patel, J. Am. Chem. Soc. 96, 7376 (1974).

[50] E. M. Engler, F. B. Kaufman, D. C. Green, C. E. Klots, and R. N. Compton, J. Am. Chem. Soc. 97, 2921 (1975).

[51] See for example, J. S. Miller and A. J. Epstein, Prog. Inorg. Chem. 20, 1 (1975).

[52] R. P. Messmer and D. R. Salahub, Phys. Rev. Lett. 35, 533 (1975).

[53] R. M. Metzger, J. Chem. Phys. 57, 1870 (1972).

[54] R. M. Metzger (private communication).

[55] C. E. Klots, R. N. Compton, and V. F. Raaen, J. Chem. Phys. 60, 1177 (1974).

[56] We use the molecular charge distributions from Ref. 8 for TTF^+ and TCNQ^- (Qs from Table V) shown in Table III.

[57] F. B. Kaufman and D. C. Green (private communication); values obtained by electrochemical comparison of NMP, TTF, and TMPD in solution.

[58] *Handbook of Chemistry and Physics*, 42nd ed. (Chemical Rubber, Cleveland, 1960), p. 2549.

[59] T. J. Kistenmacher, T. E. Phillips and D. O. Cowan, Acta Crystallogr. B 30, 763 (1974).

[60] C. J. Fritchie, Jr., Acta Crystallogr. 20, 892 (1966).

[61] M. Konno and T. Saito, Acta Crystallogr. B 30, 1294 (1974).

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

[63] I. Shirotani and H. Kobayashi, Bull. Chem. Soc. Jpn. 46, 2595 (1973).

[64] H. Kobayashi (unpublished).

[65] T. Sundaresan and S. C. Wallwork, Acta Crystallogr. B 28, 491 (1972).

[66] R. L. Bush, Phys. Rev. B 12, 5698 (1975).

[67] R. M. Metzer (private communication).

[68] B. D. Silverman, W. D. Grobman, and J. B. Torrance (unpublished).

[69] For example, L. B. Coleman, M. J. Cohen, D. J. Sandman, F. G. Yamagashi, A. F. Garito, and A. J. Heeger, Solid State Commun. 12, 1125 (1973); A. A. Bright, A. F. Garito, and A. J. Heeger, Phys. Rev. B 10, 1328 (1974).

[70] F. Denoyer, R. Comès, A. F. Garito, and A. J. Heeger, Phys. Rev. Lett. 35, 445 (1975).

[71] S. Kagoshima, H. Anzai, K. Kajimura, and T. Ishiguro, J. Phys. Soc. Jpn. 39, 1143 (1975).

[72] H. A. Mook, and C. R. Watson, Jr., Phys. Rev. Lett. 36, 801 (1976).

[73] R. Comès, S. M. Shapiro, G. Shirane, A. F. Garito, and A. J. Heeger, Phys. Rev. Lett 35, 1518 (1975).

[74] D. J. Klein, W. A. Seitz, M. A. Butler, and Z. G. Soos (unpublished); Z. G. Soos (private communication); and Ref. 2.

[75] J. B. Torrance, Y. Tomkiewicz, and B. D. Silverman (unpublished).

[76] M. A. Butler, F. Wudl, and Z. G. Soos. Phys. Rev. B 12, 4708 (1975).

[77] J. F. Kwak, G. Beni, and P. M. Chaiken, Phys. Rev. B 13, 641 (1976).

[78] Y. Tomkiewicz (unpublished).

[79] J. A. Stratton, *Electromagnetic Theory* (McGraw-Hill, New York, 1941), p. 146.

[80] It has been pointed out (Ref. 9) that $E_M(\rho)$ is not exactly proportional to ρ^2, due to the finite quadripole moments of the neutral molecules. For TTF-TCNQ, however, the calculations (Ref. 8) of $E_M(\rho)$ show that the

departures from the ρ^2 behavior are very small.

[81] It is suggested in Ref. 8 that the second term of Eq. (2) is not simply linear in ρ.

[82] Here we do not discuss possible contributions to ρ arising from virtual change transfer (*i.e.*, covalency or hybridization) between stacks.

[83] R. E. Merrifeld, Phys. Rev. Lett. 34, 877 (1975).

[84] J. J. Chang, S. Jafarey, and D. J. Scalapino, Phys. Rev. B 12, 5560 (1975).