

THE C-AXIS INTERACTION IN $(\text{TMTSF})_2\text{X}$

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Résumé — Nous avons calculé l'intégrale de transfert suivant la direction c dans $(\text{TMTSF})_2\text{ReO}_4$ et nous trouvons une valeur d'environ 1 meV. Nous comparons ce résultat avec les données de champs critiques et discutons les conséquences sur les mesures d'oscillations quantiques et sur l'ordre des anions selon l'axe c .

Abstract — We have calculated the c -axis transfer integral in $(\text{TMTSF})_2\text{ReO}_4$ and find a value of approximately 1 meV. We compare this result with critical field data and discuss its implications for quantum oscillation measurements and c -axis anion ordering.

1. Introduction.— It is generally believed that the electronic interactions in $(\text{TMTCF})_2\text{X}$ in the c -axis direction are small; however, very little in the way of quantitative measurement or theoretical estimate of this coupling exists. In this short paper, we give a limited calculation of the major c -axis transfer integral for $(\text{TMTSF})_2\text{ReO}_4$. By the term limited, we mean the TMTSF methyl groups were replaced by hydrogen in the usual attempt to optimize computational efficiency. However, unlike the electronic properties along the a and b directions in $(\text{TMTCF})_2\text{X}$ [1], the dispersion along c may depend strongly on the presence of the methyl groups. Therefore, our calculation here should be considered preliminary and a lower limit to what the actual interaction might be.

2. Transfer integral calculation.— The calculational method employed was the semi-empirical Mulliken-Wolfsberg-Helmholtz (MWH) technique[2] with an extended multi- ζ atomic basis set[3]. The dimer splitting of the HOMO level of the complex in question was taken to be twice the requisite transfer integral. Two different intermolecular complexes were studied—one consisted of the nearest neighbor TMTSF pair in the c -direction, and the other comprised a $\text{TMTSF}-\text{ReO}_4-\text{TMTSF}$ triad containing the closest O—S contacts to be found in the compound. The latter case is shown in Figs. 1 and 2. Figure 1 displays $(\text{TMTSF})_2\text{ReO}_4$ in its anion ordered state. Note that, due to symmetry considerations, the transfer integral for nearest O—S coupling will be the same at each of the two anion positions. Figure 2 contains the top view of the lower triad of Fig. 1. We chose ReO_4 as the anion in our calculation because almost any other choice would have necessitated the use of virtual d -orbitals on the central metal atom to achieve the required ligand bond symmetry. The metal atoms of these anions are heavily oxidized by their ligands, a situation favoring strong mixing of d -like symmetry into the anion molecular orbitals[4]. Virtual d -orbitals present a significant formal problem to the MWH technique; however, rhenium, which possesses occupied $5d$ states, is readily accommodated.

3. Results and conclusions.— The closest direct cation-cation distance results from a simple translation along the c -axis plus an inversion. The transfer integral linking this pair was found to be less than 0.02 meV. It is doubtful that actual inclusion of the methyl groups would increase this value significantly. Thus, for all practical purposes, one can neglect any direct electronic interaction between cations along the c -direction. On the other hand, for the indirect interaction via an ReO_4 anion as pictured in Fig. 2, we obtained a transfer integral magnitude close to 1 meV. Greene, *et al.*[5], have measured the critical field anisotropy in the b^*-c^* plane of $(\text{TMTSF})_2\text{ClO}_4$. From these data, one can determine the coherence length anisotropy in an effective mass model. They find $\xi_b/\xi_c \approx 20$. For either diffusive transport, or coherent transport involving open Fermi surfaces[1],

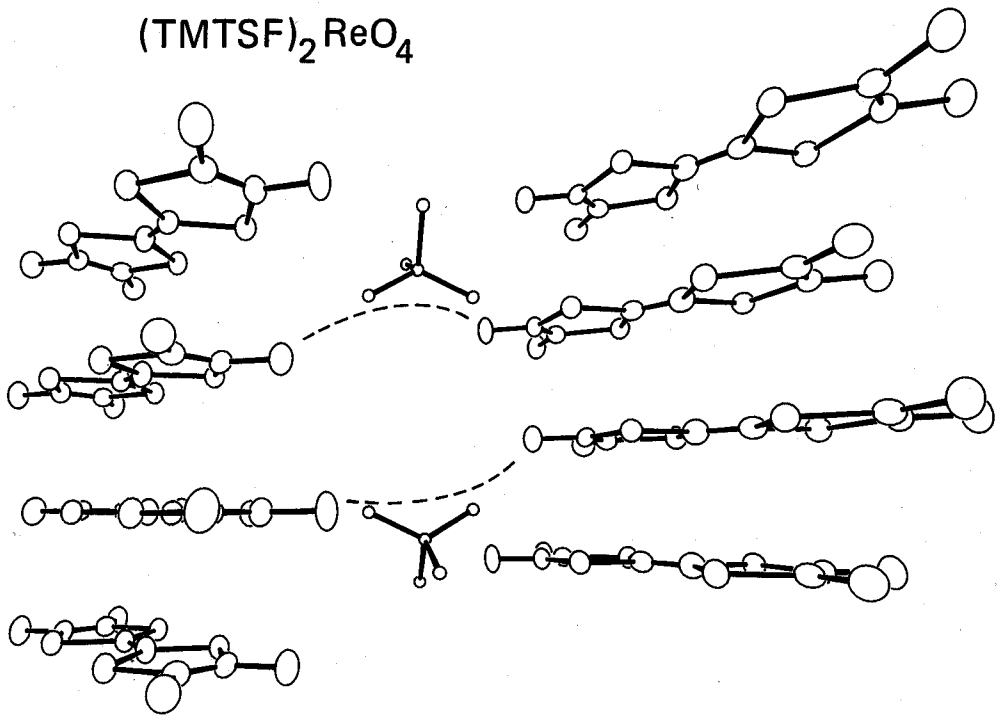


Fig. 1. The cation-anion-cation c-axis interaction seen in perspective in $(\text{TMTSF})_2\text{ReO}_4$. The anions are shown in their low temperature ordered positions. The two most closely coupled triads are indicated by the dashed lines. The lower triad was actually the one used for the calculation reported here. The upper triad is related to the lower by inversion symmetry. The atomic coordinates were obtained from G. Rindorf (private communication).

the various components of the coherence length are proportional to an associated transfer integral. Since the average transfer integral in the b-direction in $(\text{TMTSF})_2\text{X}$ is around 23 meV[1], applying the critical field result yields a c-axis transfer integral very close to our calculated value. It would appear that our replacement of each methyl group by a hydrogen is reasonable, but nonetheless this approximation must actually be checked. The small, but finite, c-axis transfer integral has several implications. First of all, it is large enough to support coherent transport below 10K where magneto-oscillation experiments[6] have been performed. Chaikin, *et al.*[7], have pointed out that when the Landau level spacing exceeds the bandwidth in the direction of the applied magnetic field, one can get quantum oscillations in the magnetic and transport response functions in the absence of closed Fermi contours. Essentially, the state space integration of the partition function in the diamagnetic free energy takes on a qualitatively different character for narrow bands than for an infinite continuum. On the other hand, it is small enough to be overcome by Madelung potentials introduced by anion ordering along c, and perhaps even by that component of the antiferromagnetic exchange along the same direction. That is, any potential introduced by these two ordering

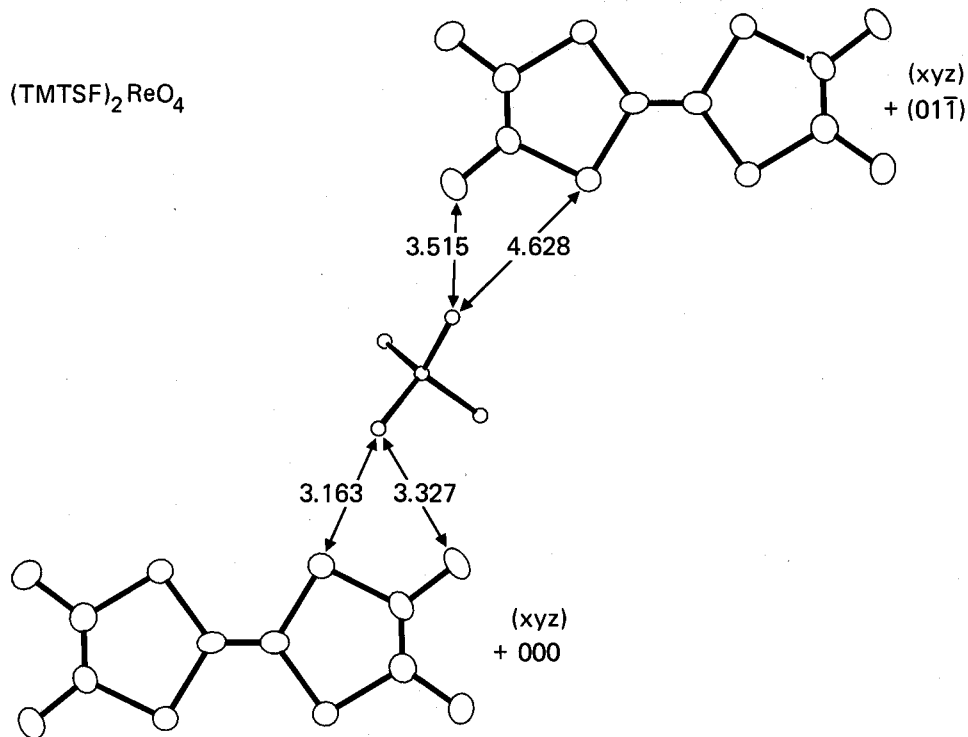


Fig. 2. The cation-anion-cation c-axis interaction seen in b-c plane projection in $(\text{TMTSF})_2\text{ReO}_4$ with closest cation-anion contacts designated. The particular projection is that of the lower triad in Fig. 1.

mechanisms is likely to <<gap>> the Fermi surface over the entire b^*-c^* plane. Thus, the insulating nature of the $Q = (0, 1/2, 1/2)$ phase observed in $(\text{TMTTF})_2\text{SCN}[8]$ may actually arise from this mechanism.

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References

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