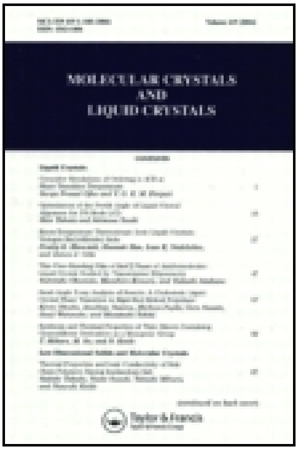

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DISPERSION OF THE POLARIZABILITY TENSOR BY INTER- AND INTRASTACK EXCITATIONS IN ORGANIC CONDUCTORS*

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Abstract In $(TMTSF)_2FSO_3$ a rotation of the polarizability tensor on the stack axis by about 30° is observed in the VIS. The polarizability is governed by the polarizability parallel to the long axis of the TMTSF molecules. The interstack Se-Se contacts are orientated symmetrically referring to the TMTSF molecules. Nevertheless intramolecular excitations may lead to the observed rotation due to the simultaneous excitation along the shortest Se-anion contact. This contact is perpendicular to the stack but inclined to the long axis of the TMTSF molecules. - In $(BEDT\cdot TTF)_2I_3$ there are more interstack contacts yielding to two-dimensional properties. The interstack S-S contacts are also arranged symmetrically. No dispersion of the polarizability tensor is observed.

$(TMTSF)_2FSO_3$

Previous measurements[1] of the orientation of the polarizability tensor in $(TMTSF)_2FSO_3$ are confirmed. The direction X of minimum polarizability is found always parallel to the stack direction, or [100]. At ≈ 20000 cm^{-1} the direction Z of maximum polarizability is approximately parallel to the longitudinal axes L of the TMTSF molecules. Going to lower frequencies (≈ 15000 cm^{-1}) the polarizability tensor revolves on the stack direction, or X, by about 30 degrees. Figure 1 shows the measured angle $\measuredangle(Z,L)$ between Z and L. The same behavior in this spectral range is also found for $(TMTSF)_2ClO_4$.

The relative birefringence in the observed spectral range 5000 - 25000 cm^{-1} is also plotted in Figure 1 showing the excitations in $(TMTSF)_2FSO_3$. The principle indices of refraction n_β and n_α correspond to the direction of the intermediate and minimum

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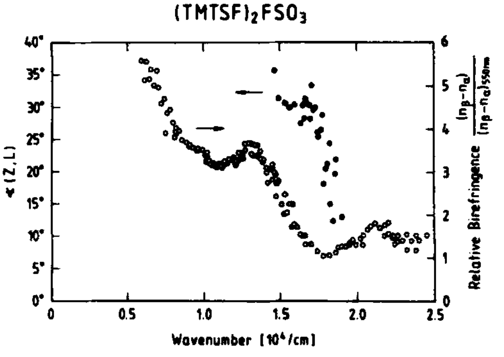


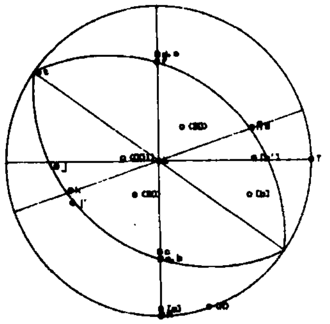
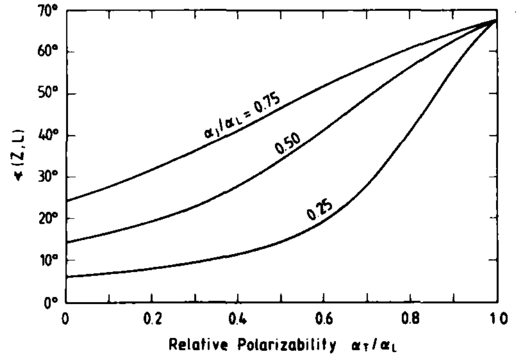


FIGURE 1 Rotation of the polarizability tensor and intramolecular excitations measured in $(TMTSF)_2FSO_3$.
● angle $\sphericalangle(Z,L)$, o relative birefringence $(n_\beta - n_\alpha)/(n_\beta - n_\alpha)_{550\ nm}$

FIGURE 2 Directions of the intrastack (a-f) and the interstack (g,h,k,t) Se-Se contacts in $(TMTSF)_2FSO_3$ in stereographic projection related to the TMTSF molecule. L longitudinal axis, T transversal axis, and N normal of the TMTSF molecule. j shortest Se-anion contact. (30) poles of planes inclined by 30° to L.

polarizability respectively.

The reason for the rotation of the polarizability tensor is the combination of the polarizability of the Se-anion contact and of the intramolecular excitations in TMTSF. Figure 2 illustrates in a stereographic projection the directions of the different Se-Se contacts in the $(TMTSF)_2FSO_3$ crystal calculated from atom coordinates[2]. Surprisingly the directions of the Se-Se contacts are arranged in a symmetrical 60° network related to the TMTSF molecule. In Figure 2 L stands perpendiculary. The stack direction, or a, points downwards. All directions of the intrastack Se-Se contacts (a-f) lie in the plane (L,a) symmetrically to L with $\sphericalangle(L,(a,b,c)) \approx \sphericalangle(L,(d,e,f)) \approx 68^\circ$. Also the directions of the interstack Se-Se contacts g,h,k lie in a plane (R) symmetrically to L with $\sphericalangle(L,k) \approx \sphericalangle(L,(g,h)) \approx 68^\circ$. The pole (R) of this plane is inclined to the stack direction $\sphericalangle(\text{stack}, (R)) \approx 18.6^\circ$. This angle



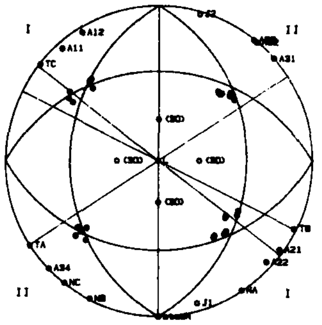


FIGURE 3 Calculated angel $\measuredangle(Z,L)$ against relative polarizability α_T/α_L for different parameters α_j/α_L. α_T, α_L, α_j polarizabilities in the directions T, L, and j, respectively.

FIGURE 4 ● directions of the intrastack (A_{ij}) and interstack S-S contacts in α-(BEDT-TTF)$_2$I$_3$ in stereographic projection related to L and stack. L longitudinal axes, TA, TB, TC transversal axes, NA, NB, NC normals of the BEDT-TTF molecules A, B, and C, respectively. J_1, J_2 longitudinal directions of the iodine molecules.

changes remarkably with different anions and decreases with lowering temperatures (e.g. ≈ −14 % for (TMTSF)$_2$ ReO$_4$ at 120 K). The interstack Se-Se contact t stands perpendiculary to L on the bisector of the angle between the planes (L,a̲) and (R). The directions of all Se-Se contacts lie in planes (30) inclined by 30° to L. The angles are $\measuredangle(t,(d,e,f)) \approx \measuredangle((d,e,f),(g,h)) \approx \measuredangle(t,k) \approx \measuredangle(k,(a,b,c)) \approx 60^\circ$.

Only the Se-anion contact j lies unsymmetrically in the plane (L,T) inclined to L. Therefore the observed rotation of the polarizability tensor is due to the combination of the polarizability in direction j with intramolecular excitation in TMTSF. In Figure 3 the calculated angle $\measuredangle(Z,L)$ is plotted against the relative polarizability α_T/α_L (α_T, α_L, α_j polarizabilities in directions T, L, and j, respectively). Variation of α_T/α_L by intramolecular excitations yields variation of the angle ∡(Z,L).

α-(BEDT-TTF)$_2$I$_3$

A rotation of the polarizability tensor in α-(BEDT-TTF)$_2$I$_3$ is not observed due to the symmetric arrangement of the contacts. The direction Z of maximum polarizability is fixed parallel to L.

Figure 4 shows the directions of the S-S contacts in α-(BEDT-TTF)$_2$I$_3$ calculated from crystal data[3]. The longitudinal axes L of all three molecules A, B, C have the same direction (⊥ stack). There are 4 intrastack S-S contacts between adjacent molecules. These contacts (A_{ij}) lie perpendiculary and symmetrically to L, also the longitudinal directions J_1 and J_2 of the iodine molecules. There are 7 interstack S-S contacts between adjacent molecules. These contacts form a 60° network symmetrically to L. The contacts are directed parallel to the intersecting lines of the 30° inclined planes (30). This demonstrates the fixed position of the polarizability tensor and also the two-dimensionality of this material.

The Se-Se (or S-S) contacts are built up in a 60° network symmetrically to the longitudinal axes L of the molecules. The base of the network is the intramolecular Se-Se distance (e.g. 3.39 ... 3.41 Å in (TMTSF)$_2$X). If the intramolecular distance becomes too small mixing of parallel and 60° networks results.

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