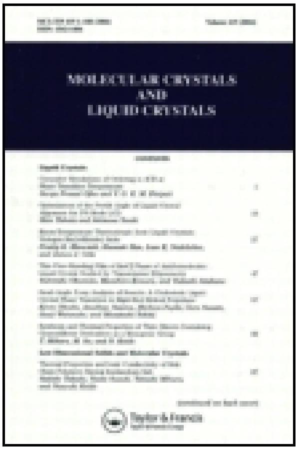

Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

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Version of record first published: 17 Oct 2011.

To cite this article: M. Miljak & J. R. Cooper (1985): Magnetic Anisotropy of $(TMTSF)_2ClO_4$ in Relaxed and Quenched States, Molecular Crystals and Liquid Crystals, 119:1, 141-146

To link to this article: http://dx.doi.org/10.1080/00268948508075148

Mol. Cryst. Liq. Cryst. 1985, Vol. 119, pp. 141-146
0026-8941/85/1194-0141/$15.00/0

Printed in the United States of America

MAGNETIC ANISOTROPY OF $(TMTSF)_2ClO_4$ IN RELAXED AND QUENCHED STATES

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Abstract - Measurements of magnetic anisotropy of single crystals of $(TMTSF)_2ClO_4$ have been made from 2-300K for the relaxed (R) and quenched (Q) states. In the R state the principal axes of the susceptibility tensor coincide with the TMTSF axes and the anisotropy is dominated by the molecular diamagnetism. Small changes below 30K are ascribed to anion ordering at T_A=25K. Above T_A there is a small temperature dependence which is shown to arise from the spin susceptibility (χ_s) via the g factor anisotropy. This effect can be used to make a new estimate of χ_s. In the Q state measurements well below the spin flop field of 3.1 kg give the direction of the antiferromagnetic easy axis which is 42° out of the molecular plane (towards a) and at 73° to the long molecular axis.

In this paper we report new results of torsion measurements made on an 800 μg single crystal of $(TMTSF)_2ClO_4$ in a uniform magnetic field (H) using a quartz fibre torque meter (M.Miljak to be published). The torque was measured as a function of H and field angle (θ) for several crystal orientations. The R state was obtained by cooling slowly, in about 30 minutes, from 77 to 4.2K while the Q state corresponds to a cooling time of 30 secs from 45 to 4.2K.

Some typical anisotropy results for the R state are shown in Figure 1(a). The conversion factor from torque in dyne cm to anisotropy in susceptibility ($\Delta\chi$) in emu/mole is 1/8.4 ie. depending on the crystal orientation the magnitude of $\Delta\chi$ ranges from $4\cdot10^{-5}$ to $1\cdot10^{-5}$ emu/mole and is mostly due to the anisotropy in the temperature independent molecular diamagnetism.

The results in 1(a) for H in the plane perpendicular to a agree with those reported previously[1]. For other orientations the differences are due to the different crystal morphology (in ref.1 the

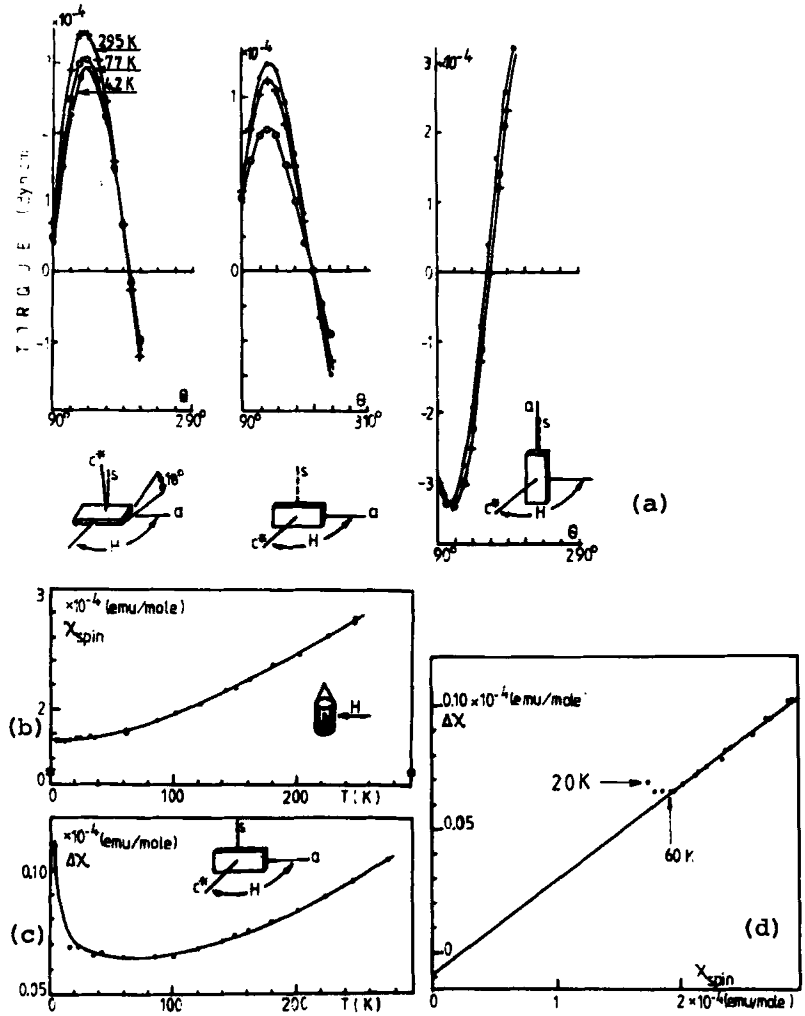

Fig. 1. Anisotropy and susceptibility results for (TMTSF)$_2$ClO$_4$ in the relaxed state.

(a) Torque versus field angle at 5 kgauss for the three crystal orientations shown. S shows the direction of the quartz suspension and ←H→ the field plane.

(b) Spin susceptibility vs. temperature using a constant core diamagnetism -4.07 10^{-4}emu/mole ((TMTSF)$_2$ClO$_4$)

(c) Anisotropy (Δχ) in ac* plane vs. temperature

(d) Anisotropy (Δχ) versus spin susceptibility for temperatures between 280 and 4.2K.

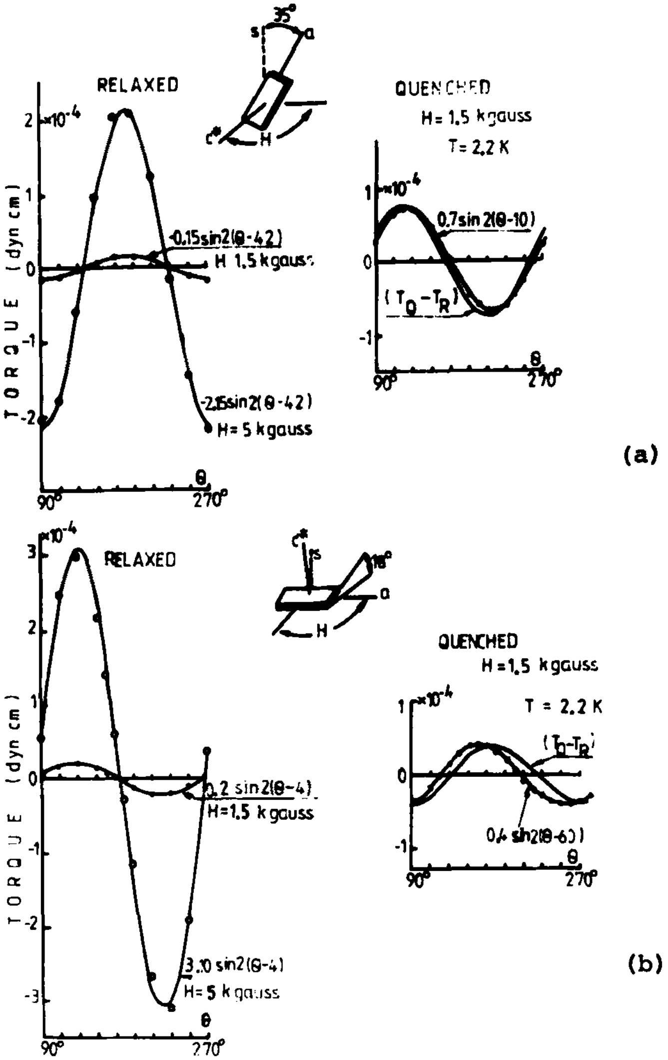

Fig. 2. Comparison of anisotropy of (TMTSF)$_2$ClO$_4$ in the relaxed (R) and quenched (Q)states for two special orientations exhibiting a spin flop anomaly at 3.1 kgauss.

(a)Sample rotated 35° about c.At H=1.5kgauss the amplitude of the sine curve is 5 times larger in the Q state.One of the crossing points of the T_Q-T_R curve at 81° to c* corresponds to H very near to the antiferromagnetic easy axis.*

(b)Sample rotated 18° about a.Again the crossing point of T_Q-T_R which is at 42° to a closely corresponds to the easy axis.

largest face was in fact an $(0\bar{1}1)$ plane ie. the plane containing $\underline{a}$ and the longest molecular axis whereas in the present work it is an $(0\,0\,1)$ plane). For H‖ $\underline{a}$ there is a small shift in the sine curve below 30K which is ascribed to the anion ordering at T_A=25K.We have seen similar, but somewhat larger, shifts in the ReO_4 and FSO_3 analogues. For the other two crystal orientations shown in Figure 1(a) the amplitude of the torque curves changes slightly with temperature. In Figures 1(b) and 1(c) we compare the temperature dependence of the spin susceptibility[1] and the anisotropy ($\Delta\chi$) in the ac^* plane. They are very similar, and as shown in Figure 1(d) they are in fact linearly related to each other between 280 and 60K. The slope of the line, $\Delta\chi/\chi_s$, in Figure 1(d) is equal to what would be expected from the known anisotropy[2] in the temperature independent conduction electron g factor, namely $g^2_{c^*} - g^2_a/<g^2>$ to within 6%. So the torque curves contain a small term arising from the anisotropy in the conduction electron susceptibility which is proportional to $\chi_s \cdot \delta g^2/<g^2>$. This holds down to at least 60 K (and possibly 30K) and provides a new way of estimating χ_s.

From the intercept of the straight line in Figure 1(d) with the χ_s axis we see that the values of χ_s are $0.2 \pm 0.05 \cdot 10^{-4}$ emu/mole too high. Thus the correct value of $\chi_s(60)$ is $1.7 \pm 0.05 \cdot 10^{-4}$ emu//mole which is 21% larger than the estimate given previously[1].

In Figure 2 are shown torque (T) curves versus field angle in the R and Q states at 1.5 kgauss - well below the spin flop field, and where even in the antiferromagnetic state the susceptibility tensor will be approximately field independent. The difference curves T_Q-T_R are shown because these give information about the anisotropy caused by the antiferromagnetism. In the Q state at 1.5 kgauss the amplitudes of the sine curves are factors of 5 (Figure 2(a)) and 2 (Figure 2(b)) larger than in the R state.Thus in the Q state the anisotropy is of the order of $0.8\text{-}1.4 \cdot 10^{-4}$ emu/mole, corresponding to the partial disappearance of the spin susceptibility along the easy axis.

For the special crystal orientationsin Figure 2 there are clear anomalies at the spin flop field of 3.1 kgauss as shown in Figure 3. A detailed analysis of these results is under way to compare them with the torsion results for the PF_6 salt[1] and the antiferromagnetic resonance work by Torrance and coworkers[3]. In general the zero crossing points of the T_Q-T_R sine curves do not correspond to the principal axes. However for the orientationsshown there are also clear spin flop anomalies close to some of the crossing points (Figure 3). Thus the crossing point in Figure 2(a) at an angle of 81° to c* and that in Figure 2(b) at an angle of 42° to a must closely correspond to the easy axis. However a careful numerical analysis is necessary to evaluate the accuracy of these estimates and the quantitative agreement with the results of ref.3.

The different amplitudes of the T_Q-T_R sine curves in 2(a) and 2(b) show that there are also large differences between the intermediate and hard axis susceptibilities. The presence of a sharp spin flop anomaly, and the similarity of the curves in Figure 3(b) with those for the PF_6 salt[1] indicate that the Q state is rather uniform even though only modest quenching speeds could be employed in this work.

In Figure 3(a) there is a "notch" anomaly at the spin flop field whereas in Figure 3(b) there is a "step". We have observed similar types of anomaly in the PF_6 salt and believe that the two different shapes may be a trademark of the easy-intermediate and easy-hard planes respectively. However a rigorous quantitative analysis of such curves is not presently available.

As indicated in Figure 4, in contrast to the AsF_6[4] and PF_6[3] salts, in quenched ClO_4 the antiferromagnetic easy axis does not seem to correspond to any particular symmetry direction, neither with respect to the crystal axes nor with respect to the molecular symmetry axes.

We are grateful to K.Bechgaard (Copenhagen) and A.Moradpour (Orsay) for the single crystal used in this study.

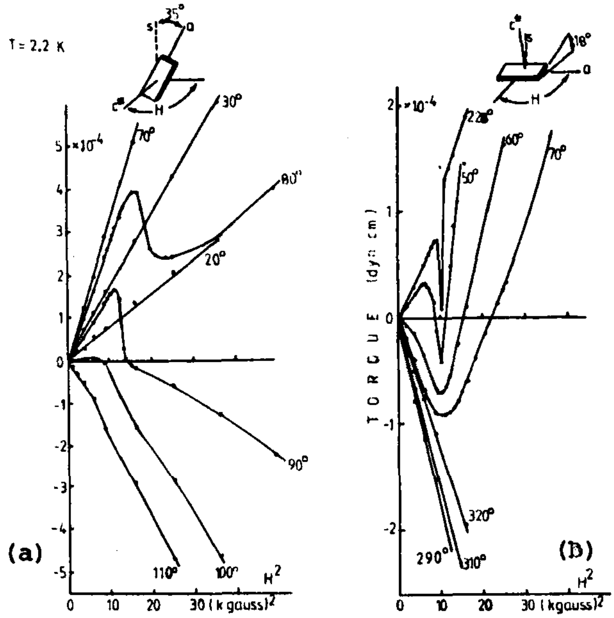

Fig. 3. Torque versus field curves for two special crystal orientations where sharp anomalies due to the spin flop transition are seen, at fields near 3.1 kgauss, and direction close to the antiferromagnetic easy axis. The H^2 dependence at low fields shows that the susceptibility tensor is constant in that region.

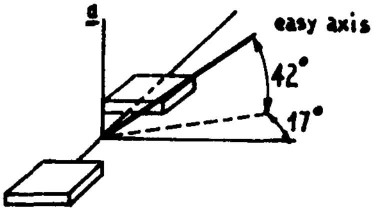

Fig. 4. From the previous figures we deduce that the easy axis has the direction shown.

REFERENCES

1. M.Miljak, J.R.Cooper and K.Bechgaard, J.Physique Coll.C3-893 44 (1983)
2. S.Flandrois et al, Mol.Cryst.and Liq.Cryst.79(1/4) 307(1982) see also H.J.Pedersen, J.C.Scott and K.Bechgaard,Phys.Rev. B24 5014 (1981)
3. J.B.Torrance, J.Physique C3-799 44 (1983) and W.Walsh et al, Phys.Rev.Lett.49 889 (1982)
4. K.Mortensen, Y.Tomkiewicz and K.Bechgaard, Phys.Rev.B25 3319 (1982)