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SDW VECTOR AND AMPLITUDE IN \((\text{TMTTF})_2 \text{SbF}_6\) AND \((\text{TMTST})_2 \text{ClO}_4\) BY NMR AND ANISOTROPY BY EPR

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Abstract. – By NMR, the nesting vector \(\mathbf{Q}\) and amplitude \(d\) of the SDW state in the organic conductors with sulfur \((\text{TMTTF})_2 \text{SbF}_6\) and selenium \((\text{TMTST})_2 \text{ClO}_4\) are respectively \(Q = -0.05b^*\) and 0.12\(b^*\) and \(d = 0.18\) and 0.12 \(\mu_B\). By EPR the, up to this date, unknown orientation of easy axis has been determined toward crystal axis \(a\) in agreement with the theory of anisotropy.

Introduction

The interplay of different phases transitions in organic conductors, such as superconductivity and antiferromagnetism is very important to the understanding of these systems. Up to this date, only N.M.R. has given information on the microscopic parameters of the antiferromagnetic SDW (spin density wave) of the sulfur and selenium organic conductors such as nesting vector \(\mathbf{Q}\) and order parameter \(d\). The sulfur compounds are more localized than the selenium compounds, and for this reason it could be thought that the order parameter is larger in sulfur compounds than in selenium compounds. In this paper our experimental results show that the order parameter and \(Q\) vector are in the same range in compounds with these two types of molecules independently of the level of apparent localization, although the order parameter is slightly larger in the sulfur compound. This shows that the amplitude of spin fluctuations in these compounds is roughly independent of level of localization.

Experimental results

In the normal state the nuclear magnetic resonance (NMR) of protons of the four methyl groups of the TMTXF molecules [1] gives superposed for each methyl: one central line and two satellite lines with dipolar shifts function of orientation of the field with respect to the normal of methyl plane. In order to obtain well resolved lines, it is absolutely necessary to use well oriented single crystals.

In the SDW state the lines are shifted by the local fields associated to the magnetic ordered structure; these fields (around 20 Gauss) are different for each methyl and larger than normal line shifts giving complex line shape varying with the orientation of the magnetic field \(H\) with respect to the single crystal orientation. In these compounds, one electron is removed for two molecules, and thus in the metallic state the nesting at the Fermi surface along the stacking axis \(a\) of the organic molecules gives \(Q_a = 1/2a^*\) and in the insulating state the completely localized limit gives the same \(Q_a = 1/2a^*\) with the sequence +0−0+0− with one electron with magnetization \(\mu_B\) for two molecules. This sequence gives eight different local fields and this relatively large number of fields give NMR lineshape not very different from the incommensurate case. Even in the localized limit the quantum spin 1/2 fluctuations decrease strongly the local magnetization. Another possibility, more symmetrical, with a sequence + + − − + + − − gives four local fields with NMR lineshapes very different from the incommensurate case. Our experimental results shows that this sequence never occurs.

The SDW structure along the \(b\) axis is less known, the NMR lines being function of the value of the component \(Q_b\) along \(b\). The calculation of the local dipolar fields needs to know the orientation (or easy axis) of the magnetization \(S\) of the SDW. A complete NMR analysis is able to determine these axis but it is much more simple to determine them by EPR antiferromagnetic resonance (EPR AFR). This has been already made [3], but in the past these EPR experiments have not been sufficiently careful, to distinguish the \(a\) and −\(a\) directions which are not equivalent, on single crystals. The analysis of the NMR results leads to different \(Q_b\) values as function of the deviation of the easy axis \(S\) from the axis \(b^*\) toward \(a\) or −\(a\), symmetrical with respect to the value \(Q_b = 0.176\). For this reason, the EPR AFR has been made on the same well oriented good single crystals used for NMR.

The EPR AFR obtains that the easy axis is oriented toward +\(a\) with angles shown in figure 1, the deviation from \(b^*\) being 36° for \((\text{TMTSF})_2 \text{ClO}_4\) and 26° for \((\text{TMTTF})_2 \text{SbF}_6\).

The NMR analysis is complicated by the existence of hyperfine fields of the same order as the dipolar fields, different for each methyl groups and different in each compound. For these compounds, we have

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rotated the magnetic field perpendicularly to the easy axis s, so that the hyperfine fields shifts are zero [2]. The comparison of theoretical and experimental results shows that the $Q_b = 0.12b^*$ for (TMMTSF)$_2$ClO$_4$ and incommensurate with a order parameter $d = 0.12 \mu_B$. For (TMNTTF)$_2$SbF$_6$ we find $Q_b$ near zero and $d = 0.18 \mu_B$.

**Anisotropy**

Our simple theory of the anisotropy [4] in these organic conductors, using the dipolar interactions and the spin orbit coupling (which is negligible in sulfur compounds but of the same order as the dipolar in the selenium compounds) explains the permutation of the intermediate and hard axis observed experimentally between the sulfur and selenium compounds. The predictions of the orientation of these axis is presented in figure 1 and compared with our experimental results. The orientation of easy axis toward axis a away from b for SbF$_6$ corresponds to $Q_b$ near zero as observed in our experiments by NMR, in complete agreement with the theoretical predictions for anisotropy.

The sulfur compounds with other counterions like AsF$_6$ or PF$_6$ have no SDW groundstate but spin Peierls state with singulet pairing. We observe that the critical temperature for SDW state decreases experimentally with the increase of $Q_b$ (observed by NMR for SbF$_6$ and deduced from the RPE orientation of the easy axis angle from b direction for SCN and Br counterions). A very simple possible explanation can be related to the ratio of transverse hopping frequency $t_b$ and $t/\left(b - a/2\right)$ to the transverse nearest neighbours in the plane (ab) which determines the nesting vector in the delocalized limit or the ratio of the two transverse AF exchange frequencies in the localized limit. $Q_b = b^*/2$ corresponds to only one exchange frequency along b, and with the simple localized sequence $+0+-0+0$ along a, we obtain one dimensional lines $+-+-+-+$ along b separated by chains of neutral molecules o, so that a commensurate spin Peierls distortion can occurs on these one dimensional AF structure, giving singulet pairs. The unique exchange frequency along b favors such singulet pairs, separated from the others along a by neutral molecules.

On the contrary, when $Q_b = 0$ the two transverse hopping frequencies are of the same order, destroying the $+0-0+$ ordering along adjacent chains, because there is always an hopping term from one ionised molecule to a neutral molecule; this frustration of exchange suppress the possibility of formation of singlets pairs in the transverse direction leaving only an AF order along the a direction. This simple argument can explain the experimental separation in sulfur compounds between SDW state and spin Peierls as function of $Q_b$ vector or the ratio of transverse exchange frequencies. A more complex delocalized model will necessarily preserve this tendency on short range, by resonance between the different configurations.

**Conclusion**

We have determined the microscopic parameters of the organic conductors by NMR and EPR. The results are in agreement with the theory of anisotropy in sulfur compounds.