Exploring the Charge-Ordering Transition in (TMTTF)$_2$X via Thermal Expansion Measurements

Mariano de Souza$^a$, Daniel Hofmann$^a$, Pascale Foury-Leylekian$^b$, Alec Moradpour$^a$, Jean-Paul Pouget$^b$, Michael Lang$^a$

$^a$Physikalisches Institut, Goethe-Universität Frankfurt, SFB/TRR 49, D-60438 Frankfurt (M), Germany
$^b$Laboratoire de Physique des Solides, Université Paris Sud, CNRS UMR 8502, Orsay, France

Abstract

We report results of high-resolution measurements of the $c'$-axis expansivity ($\alpha_{c'}$) at the charge-ordering (CO) transition for the quasi-1D (TMTTF)$_2$X compounds with X = SbF$_6$ and Br and make a comparison with previous results for the X = PF$_6$ and AsF$_6$ salts. For X = SbF$_6$, due to the screening of the long-range Coulomb forces, a sharp $\lambda$-type anomaly is observed at $T_{CO}$, which contrasts with the step-like mean-field anomaly at $T_{CO}$ for PF$_6$ and AsF$_6$, where CO occurs in the Mott-Hubbard charge-localized regime. For the latter two salts, a negative contribution to $\alpha_{c'}$ is observed above $T_{CO}$. This feature is assigned to the anions’ rigid-unit modes, which become inactive for $T < T_{CO}$. Our $\alpha_{c'}$ results for the X = Br salt, where such rigid-unit modes are absent, reveal no traces of such negative contribution, confirming the model based on the anions’ rigid-unit modes for the X = PF$_6$ and AsF$_6$ salts.

Key words: Charge-Ordering Transition, Ferroelectricity, Thermal-Expansion, Organic Conductors

PACS: 71.20.Rv, 71.30.+h, 65.40.De

1. Introduction

The observation of a charge-ordering (CO) transition [1] coinciding with the onset of ferroelectricity [2] in the quasi-1D conductors of the (TMTTF)$_2$X family with X = PF$_6$ ($T_{CO} \approx 65$ K [1]), AsF$_6$ ($T_{CO} \approx 105$ K [1]), SbF$_6$ ($T_{CO} \approx 154$ K [2]) salts have revealed the exceptional properties of the Mott-Hubbard insulating phase in these materials. Also for the X = Br salt, some experimental evidence for a CO transition around 50 K have been reported in the literature [3]. The CO transition has been assigned to the importance of both on-site $U$ and inter-site $V$ Coulomb interactions [4], with strong influence from electron-lattice coupling [5, 6, 7]. Actually, first indications for a CO transition in the (TMTTF)$_2$X family were observed more than twenty years ago. Resistivity measurements on the X = SbF$_6$ salt [8] revealed a sharp metal-to-insulator transition at $T_{MI} \approx 154$ K, coinciding with a pronounced change in the thermopower [10] and a peak divergence in the dielectric permittivity $\epsilon'$ [9]. The absence of signatures in the magnetic susceptibility [10] led to the belief that only charge degrees of freedom are involved in this transition. Furthermore, due to the experimental difficulties posed by detecting lattice effects associated with the CO transition [11], no evidence of structural changes [8] has been reported and, due to this, the CO transition has been labeled structureless transition. By means of ultra-high-resolution thermal expansion experiments, we recently succeeded in detecting strongly anisotropic lattice effects accompanying the CO transition for the X = PF$_6$ and AsF$_6$ salts [12]. Most importantly, for the latter salts, the strongest effects at both the charge ordering and the spin-Peierls transition [13] occur along the $c'$-axis, along which planes of (TMTTF)$_2$ molecules alternate with planes of counter anions X (X$^−$). Hence, the results in [12] provide the first experimental evidence of the role of anion displacements for the stabilization of the charge-ordered phase, in line with theoretical predictions employing the extended Hubbard model coupled to the anions [5]. Here we report on thermal expansion measurements along the $c'$-axis of (TMTTF)$_2$X with X = SbF$_6$ and Br and make a comparison with previous results for X = PF$_6$ and AsF$_6$.

2. Experimental

High-quality single crystals of (TMTTF)$_2$X with centrosymmetric anions X = SbF$_6$ and Br were grown...
from THF using the standard constant-current procedure. The uniaxial thermal expansion coefficient, \( \alpha(T) = \Gamma^{-1} (\partial l / \partial T) \), with \( l \) denoting the sample length, was measured by employing an ultra-high-resolution capacitance dilatometer with a maximum resolution of \( \Delta l/l = 10^{-10} \), built after [15]. The dilatometer used here has proven particularly useful for exploring lattice effects in organic charge-transfer salts, see, e.g. [16]. The experimental data presented were corrected for the thermal expansion of the dilatometer cell with no further data processing. The alignment of the crystal orientation was guaranteed with an error margin of \( \pm 5^\circ \).

3. Results and Discussion

In the main panel of Fig. 1 we recall the results of thermal expansion measurements along the \( c^* \)-axis for the \((\text{TMTTF})_2 \) salt with \( X = \text{PF}_6 \) [12, 13]. A similar behavior is observed for the \( X = \text{AsF}_6 \) salt [12, 13] with slight shifts in the positions of the anomalies at \( T_{\text{CO}} \) and the spin-Peierls transition \( T_{\text{SP}} \). A striking feature revealed by these experiments was the decrease of \( \alpha_{\text{C}} \) for \( T \geq T_{\text{CO}} \), at variance with an ordinary lattice expansion which monotonously increases with increasing temperatures in a more or less Debye-like manner, indicating the action of a negative contribution to \( \alpha_{\text{C}} \) in this temperature regime. In Ref. [12], this effect has been attributed to rigid-unit modes of the \( \text{PF}_6 \) and \( \text{AsF}_6 \) anions and their coupling to the charge ordering: on approaching \( T_{\text{CO}} \) from above, growing CO fluctuations, cause, via S-F contacts, positional fluctuations of the anions towards their new off-center equilibrium positions. These positional fluctuations provide an effective damping of the anions’ rigid-unit modes. Upon cooling through \( T_{\text{CO}} \), the CO becomes static, giving rise to a freezing of these vibration modes and, as a consequence, the negative contribution in \( \alpha_{\text{C}} \) is no longer active.

In Fig. 4 we show corresponding data for the \( X = \text{Br} \) salt, where no such rigid-unit modes exist. In fact, for the temperature range shown here, the data lack any indication for a negative contribution in \( \alpha_{\text{C}} \), consistent with the model proposed in [12]. Instead, \( \alpha_{\text{C}} \) shows distinct anomalies, the origin of which are not fully understood at present. This refers to the peak anomaly centered around 140 K, reproduced for the two crystals investigated here, as well as the upturn above \( \sim 180 \) K. Another remarkable aspect is that \( \alpha_{\text{C}} \) is roughly one order of magnitude smaller in the \( X = \text{Br} \) than in the \( \text{PF}_6 \) and \( \text{AsF}_6 \) salts. A possible explanation for this discrepancy as well as for the above-mentioned absence of the negative contribution to \( \alpha_{\text{C}} \) for the \( X = \text{Br} \) salt could be associated to the more dense packing of the \( X = \text{Br} \) salt along the \( c^* \)-axis. In other words, the \( \text{Br}^- \) anion fits better into the methyl group cavities [14] This leaves less possibility to a CO transition in this salt triggered by anion displacements, as it occurs in \( X = \text{PF}_6 \), \( \text{AsF}_6 \) [12].

For the \( X = \text{SbF}_6 \) salt (inset of Fig. 1), a \( \lambda \)-like negative anomaly is observed at \( T_{\text{CO}} = 154 \) K which nicely coincides with the peak anomaly in \( \epsilon \) [17]. The shape and size of the phase transition anomaly, indicative of the presence of strong fluctuations, differ markedly from the mean-field-like anomaly at \( T_{\text{CO}} \) for the \( X = \text{PF}_6 \), \( \text{AsF}_6 \) salts, cf. Fig. 1 and Ref. [12]. This difference can be understood as a consequence of short-range Coulomb forces in the \( \text{SbF}_6 \) salt, where CO coincides with a metal-insulator transition \( (T_{\text{CO}} = T_{\text{MI}}) \), implying a more effective screening of the long-range Coulomb forces above \( T_{\text{CO}} \), as compared to the \( \text{AsF}_6 \) and \( \text{PF}_6 \) salts, where \( T_{\text{CO}} < T_p \), with \( T_p \) denoting the position of the minimum in the resistivity, which marks the onset of the charge localization [21].

The negative sign of the phase transition anomaly indicates, according to the Ehrenfest relation, a decrease of \( T_{\text{CO}} \) upon applying uniaxial pressure along the \( c^* \)-
The crucial observation made here is a negative pressure dependence of $T_{CO}$ for the X = SbF$_6$ salt [13]. Hence, the present results suggest that also for the X = SbF$_6$ salt the $c^*$ lattice parameter plays an important role in the pressure-induced changes of $T_{CO}$. The results for the X = SbF$_6$ salt in the whole temperature range will be published elsewhere [23].

We turn now to the anomalous behavior of the X = Br salt at low temperatures, see main panel and inset of Fig 2. The crucial observation made here is a dramatic deviation from a Debye-like behavior in $\alpha_{c^*}$ below ~50 K, accompanied by a pronounced step-like anomaly around 17 K and a change of sign. Remarkably, according to Ref. [19], the transition into the antiferromagnetically ordered ground state of this salt takes place at 13 K, i.e. somewhat below the discontinuity in $\alpha_{c^*}$. We stress that below 17 K, a rapid drop of the $2k_F$ bond fluctuations has been reported in [20] as well as a plateau in the resistivity centered around the same temperature [21]. In addition, below $T \approx 20$ K the conductance becomes frequency dependent [22], signalizing a relaxor-type of behavior. Since a broad maximum in $\varepsilon'$ is observed in the 35-50 K temperature range [22], the possibility of the formation of a local CO and/or ferroelectric domains cannot be ruled out. Further experiments are needed to better understand the anomalous low-temperature regime of this salt.

In conclusion, by measurements of the uniaxial expansivity along the $c^*$-axis of various members of the (TMTTF)$_2$X family, distinct lattice effects accompanying the charge-ordering transition have been observed. From the different character of the phase transition anomaly for the various salts we infer the presence of short-range Coulomb forces for X = SbF$_6$, which contrasts with the longer-ranged Coulomb interactions, i.e. a reduced screening, for X = PF$_6$ and AsF$_6$. The X = Br compound lacks any indications for a negative contribution to the $c^*$-axis expansivity, which for the PF$_6$ and AsF$_6$ salts have been attributed to positional fluctuations of these anions [12].

References

[1] D.S. Chow et al., Phys. Rev. Lett. 85 (2000) 1698.
[2] P. Monceau et al., Phys. Rev. Lett. 86 (2001) 4080.
[3] C. Coulon et al., Phys. Rev. B 76 (2007) 085126.
[4] H. Sec et al., J. Phys. Soc. Jpn. 66 (1997) 1249.
[5] J. Riera et al., Phys. Rev. B 63 (2001) 241102.
[6] R.T. Clay et al., Phys. Rev. B 67 (2003) 115121.
[7] S. Brazovskii et al., Synth. Met. 137 (2003) 1331.
[8] R. Laversanne et al., J. Phys. Lett. (France) 45 (1984) L393.
[9] H.H.S. Javadi et al., Phys. Rev. B 37 (1988) 4280.
[10] C. Coulon et al., Mol. Cryst. Liq. Cryst. 119 (1985) 325.
[11] P. Foury-Leylekian et al., Physica B 312 (2002) 574.
[12] M. de Souza et al., Phys. Rev. Lett. 101 (2008) 216403.
[13] M. de Souza et al., Physica B 404 (2009) 494.
[14] J.-P. Pouget et al., J. Phys. I France 6 (1996) 1501.
[15] R. Pott and R. Schefzyk, J. Phys. E 16 (1983) 445.
[16] M. de Souza et al., Phys. Rev. Lett. 99 (2007) 037003.
[17] F. Nad et al., J. Phys. Soc. Jpn. 75 (2006) 051005.
[18] F. Zamborszky et al., Phys. Rev. B 66 (2002) 081103.
[19] S.S.P. Parkin et al., Phys. Rev. B 26 (1982) 6319.
[20] J.-P. Pouget et al., Synth. Met. 85 (1997) 1523.
[21] M. Dressel, Naturwissenschaften 94 (2007) 527.
[22] F. Nad et al., Eur. Phys. J. B 3 (1998) 301.
[23] M. de Souza et al., to be published.