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Decoupled critical dynamics of the TMTSF donor molecules in $(\mathrm{TMTSF})_2X$ organic superconductors

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We have studied a high-temperature phase transition in the organic superconductors $(\mathrm{TMTSF})_2\mathrm{PF}_6$ and $(\mathrm{TMTSF})_2\mathrm{ClO}_4$ (where TMTSF indicates tetramethyltetraselenafulvalene) by means of ^{1}H laboratory-frame and rotating-frame nuclear magnetic resonance (NMR) relaxation measurements. The ^{1}H NMR spin-lattice (T_1) and spin-spin relaxation time (T_2), representing dynamics of the TMTSF donor molecules, manifested a divergence associated with the structural phase transition at 160 K. As no anomalies were observed in the ^{19}F NMR T_1 measurements representing dynamics of the PF_6 anion, the TMTSF donor molecules and the anions are shown to be well decoupled regarding the critical fluctuations accompanying the structural phase transition.

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I. INTRODUCTION

The Bechgaard salts $(\mathrm{TMTSF})_2X$, where TMTSF is tetramethyltetraselenafulvalene, show various ground states.[1] One of them, superconductivity, has been found in $(\mathrm{TMTSF})_2X$ with monovalent inorganic anions X such as PF_6, ReO_4, or ClO_4.[2] The anions are placed in centrosymmetrical cavities confined by the methyl groups of the TMTSF molecules forming dimerized pairs. While the $(\mathrm{TMTSF})_2X$ family members are quasi-one-dimensional metals at high temperatures, their electrical conduction is known to be two or three dimensional at low temperatures.[3,4] The anion X, sitting on sites possessing an inversion symmetry, is believed to undergo rotational motions at high temperatures. The anions interact weakly with surrounding donor molecules,[5] and weak hydrogen bonds between the anions and TMTSF donor molecules are present.[6] Through competing electronic instabilities, the anion sublattice may play an important role in the rich phase diagram of the Bechgaard salts.[7]

NMR is a powerful tool for studying the lattice dynamics and microscopic environments in solids, and has been employed to a large extent in order to investigate the spin dynamics in $(\mathrm{TMTSF})_2X$ ($X=\mathrm{PF}_6,\mathrm{ClO}_4$). In particular, in a detailed study of the relaxation data, reorientation of the methyl groups has been discussed considering different environments. Besides, it was thus found that the ^{1}H NMR spin-lattice relaxation is dictated by the hyperfine coupling of the charge carriers at high temperatures above 200 K, whereas reorientation motion of the methyl groups is responsible below it as indicated by the frequency dependence of the relaxation rate.[8–10]

A structural phase transition in $(\mathrm{TMTSF})_2\mathrm{PF}_6$ has been reported in the vicinity of 160 K by x-ray measurements,[11] which revealed a change in the β angle by $\approx 1°$, associated with an interlayer shift. An unexpected high-temperature anomaly near 160 K, an abrupt increase in the temperature coefficient of resistance, has also been reported in the $(\mathrm{TMTTF})_2M\mathrm{F}_6$ compounds ($M=\mathrm{P},\mathrm{As},\mathrm{Sb}$).[12] The role of the anion motion as well as the molecular dynamics of the TMTSF donor molecules need to be understood in association with it.[12] We have been able to observe NMR and electron paramagnetic resonance as well as electrical conductivity anomalies in $(\mathrm{TMTSF})_2\mathrm{ClO}_4$, at around 160 K.[13,14] In this work, the ^{1}H NMR rotating-frame as well as laboratory-frame nuclear spin relaxation measurements were employed in order to probe the molecular dynamics associated with the TMTSF donor molecules in $(\mathrm{TMTSF})_2\mathrm{ClO}_4$ and $(\mathrm{TMTSF})_2\mathrm{PF}_6$. It is the purpose of this work to elucidate the nature of the structural phase transition at 160 K in $(\mathrm{TMTSF})_2X$ with different anions by means of the ^{1}H NMR nuclear spin relaxation measurements.

II. EXPERIMENT

Electrochemically grown samples of $(\mathrm{TMTSF})_2\mathrm{PF}_6$ and $(\mathrm{TMTSF})_2\mathrm{ClO}_4$ were investigated by using 200 MHz and 45 MHz NMR spectrometers as a function of temperature. The ^{1}H NMR spin-lattice relaxation time (T_1) was measured by the inversion recovery method, and the spin-spin relaxation time (T_2) by the solid echo decay pulse sequence.

III. RESULT AND DISCUSSION

The magnetization recovery followed a single-exponential form. Figure 1 shows the temperature dependence of the ^{1}H NMR spin-lattice relaxation rate (T_1^{-1}). A divergent behavior in the rotating-frame as well as in the laboratory-frame spin-lattice relaxation measurements is manifest in Fig. 1 at

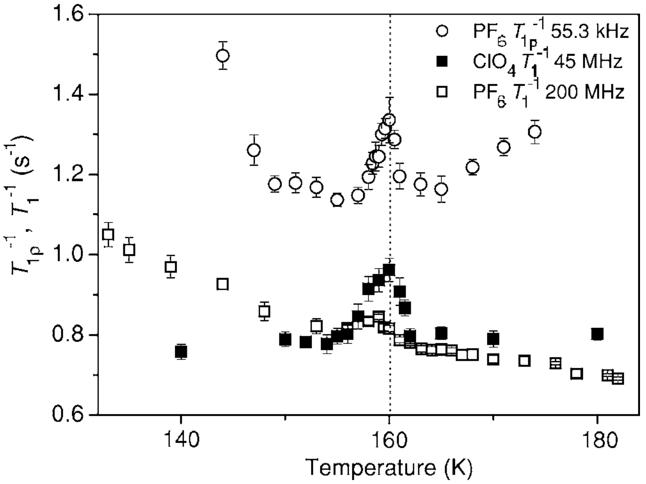

FIG. 1. Temperature dependence of the laboratory-frame and rotating-frame ^{1}H NMR spin-lattice relaxation rates in $(TMTSF)_2PF_6$ and $(TMTSF)_2ClO_4$. The dotted line is a guide to the eye.

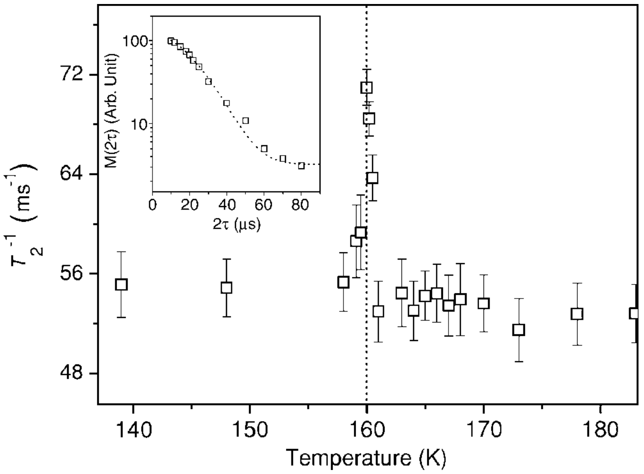

FIG. 2. Temperature dependence of the spin-spin relaxation rate in $(TMTSF)_2PF_6$. Inset: The solid echo decay pattern at 178 K, fitted by a Gaussian form.

around 160 K, which is attributed to a structural transition.[13] The methyl (CH_3) groups in the TMTSF donor molecule, being embedded in a rigid lattice, undergo a hindered rotation.[15,16] In fact, a relatively strong frequency dependence as shown in Fig. 1 indicates that the anomaly arises from molecular dynamics rather than being of an electronic origin. As the reorientational motion of the methyl groups is expected to make a significant contribution to the ^{1}H NMR nuclear spin relaxation, the critical fluctuation manifested by the divergence in the spin-lattice relaxation at 160 K can be ascribed to the structural phase transition arising from the tilting of the TMTSF donor molecules as described above. As only relatively small peaks are observed at 160 K, the structural phase transition is most likely to be of a weak first order, which may give rise to a divergence in the relaxation rate.

Figure 2 shows the temperature dependence of the spin-spin relaxation rate (T_2^{-1}) in $(TMTSF)_2PF_6$. As shown in the inset, the solid echo decay was well fitted by a Gaussian form at all temperatures, except around 160 K. The spin-spin relaxation anomaly at 160 K can also be attributed to the change in the reorientational motions of the methyl groups in the TMTSF donor molecules, arising from the structural phase transition.

While it may seem very strange to find exactly the same T_c for the PF$_6$ and ClO$_4$ salts, this in fact strongly suggests that the critical dynamics of the TMTSF donors is decoupled quite well from the anions. This point can be further supported by the ^{19}F NMR measurements of $(TMTSF)_2PF_6$.[17,18] In contrast to the case of the ^{1}H NMR nuclear spin relaxation measurements, no anomaly was found in the temperature dependence of the ^{19}F NMR spin-lattice relaxation rate probing the reorientational motions of the PF$_6$ anion molecules.[17,18]

While NMR measurements have been made in $(TMTSF)_2ClO_4$ and $(TMTSF)_2PF_6$ by various workers,[8–10] close investigation has not been done by other workers focused on the structural phase transition, in the temperature range around 160 K. We have reported NMR anomalies in $(TMTSF)_2ClO_4$ and in $(TMTSF)_2PF_6$.

In summary, the organic superconductors $(TMTSF)_2PF_6$ and $(TMTSF)_2ClO_4$ were studied by means of the ^{1}H NMR nuclear spin relaxation measurements. As a result, a structural phase transition associated with the TMTSF donor molecules was identified at 160 K, in the two systems with the same donor molecules but with different anions, whereas no anomalies associated with the anions have been observed. Thus, our work shows that the structural phase transition at 160 K for the TMTSF donor molecules in those organic superconductors takes place well decoupled from the anions.

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[1] V. J. Emery, R. Bruinsma, and S. Barisic, Phys. Rev. Lett. **48**, 1039 (1982).

[2] K. Bechgaard, C. S. Jacobson, K. Mortensen, J. H. Pederson, and N. Thorup, Solid State Commun. **33**, 1119 (1980).

[3] D. Jerome and H. J. Schulz, Adv. Phys. **31**, 299 (1982); D. Jerome, P. Auban-Senzier, L. Balicas, K. Behnia, W. Kang, P. Wzietek, C. Berthier, P. Caretta, M. Horvatic, P. Segransa, L. Hu-

bert, and C. Bourbonnais, Synth. Met. **70**, 719 (1995).

[4] A. Schwartz, M. Dressel, G. Gruner, V. Vescoli, L. Degiorgi, and T. Giamarchi, Phys. Rev. B **58**, 1261 (1998); J. Moser, M. Gabay, P. Auban-Senzier, D. Jerome, K. Bechgaard, and J. M. Fabre, Eur. Phys. J. B **1**, 39 (1998).

[5] B. Gallois, J. Gaultier, C. Hauw, and T. D. Lamcharfi, Acta Crystallogr., Sect. B: Struct. Sci. **42**, 564 (1986).

[6] J. P. Pouget and S. Ravy, J. Phys. I **6**, 1501 (1996).

[7] C. Bourbonnais, P. Wzietek, F. Creuzet, D. Jerome, P. Batail, and K. Bechgaard, Phys. Rev. Lett. **62**, 1532 (1989); K. Sengupta and N. Dupuis, Phys. Rev. B **65**, 035108 (2002); C. Coulon, P. Delhaes, S. Flandrois, R. Lagnier, E. Bonjour, J. M. Fabre, and K. Bechgaard, J. Phys. (Paris) **43**, 1059 (1982).

[8] P. C. Stein, A. Moradpour, and D. Jerome, J. Phys. (Paris), Lett. **46**, L241 (1985).

[9] P. Wzietek, F. Creuzet, C. Bourbonnais, D. Jerome, K. Bechgaard, and P. Batail, J. Phys. I **3**, 171 (1993).

[10] T. Takahashi, D. Jerome, and K. Bechgaard, J. Phys. (Paris) **46**, 945 (1984).

[11] J. C. Scott, E. M. Engler, W. G. Clark, C. Murayama, K. Bechgaard, and H. J. Pedersen, in *Proceedings of the International Conference on Low-Dimensional Conductors*, Boulder, 1981 [Mol. Cryst. Liq. Cryst. **79**, 61 (1982)].

[12] C. Coulon, S. S. P. Parkin, and R. Laversanne, Phys. Rev. B **31**, 3583 (1985).

[13] C. H. Lee, K. M. Lee, C. E. Lee, and W. Kang, Curr. Appl. Phys. **3**, 359 (2003).

[14] C. E. Lee, C. H. Lee, W. Kang, and O. H. Chung, Solid State Commun. **109**, 69 (1999).

[15] C. Choi and M. M. Pintar, J. Chem. Phys. **109**, 5542 (1998).

[16] J. C. Scott, H. J. Pedersen, and K. Bechgaard, Phys. Rev. B **24**, 475 (1981).

[17] V. J. Mcbrierty, D. C. Douglass, and F. Wudl, Solid State Commun. **43**, 679 (1982).

[18] S. H. Kim, C. H. Lee, K. W. Lee, C. E. Lee, W. Kang, and K. S. Hong, Curr. Appl. Phys. **4**, 452 (2004).