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X-RAY SCATTERING STUDY OF ONE-DIMENSIONAL CONDUCTORS TTF-TCNQ AND ITS FAMILY†

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The x-ray data obtained in the study of $TTF_{1-x}TSeF_x$-TCNQ suggest that the $2k_F$- and the $4k_F$-CDW are present predominantly on the TCNQ and the fulvalene stacks, respectively. The difference of the transverse ordering of the $2k_F$-CDW in the alloy series is discussed in terms of the Ginzburg-Landau model for the interchain interactions.

I. Introduction

Charge-density-waves(CDW) found in various kinds of quasi one-dimensional conductors have been identified simply as the $2k_F$-CDW brought about by the Peierls instability of ideal metallic-band electrons. However, the finding of the $4k_F$-CDW in TTF-TCNQ [1,2] raised a question about the simple interpretation of the origin of the CDW. It has been verified that the $4k_F$-CDW is not the usual second harmonic of the $2k_F$ [1,2] but should have its own origin. The finding of the $4k_F$-CDW has made it necessary to have advanced understanding of the origins of CDW.

We are making a systematic study of the CDW in $TTF_{1-x}TSeF_x$-TCNQ in order to clarify the relations between the origins of CDW and the electronic properties of quasi one-dimensional conductors. TSeF-TCNQ is isostructural with TTF-TCNQ. Although TTF-TCNQ has both the $2k_F$- and the $4k_F$-CDW [1,2], TSeF-TCNQ has the $2k_F$-CDW only [3,4,5]. This difference will be ascribed to the difference of the properties of the fulvalene stacks. The relation between the property of the fulvalene stack and the behavior of the $4k_F$-CDW is expected to be revealed in the study of the alloy series, and clues to clarify the origins of CDW will be obtained.

The study of the alloy series provides us with also knowledge about the interchain interaction among the $2k_F$-CDW. The $2k_F$-CDW is present in both TTF-TCNQ and TSeF-TCNQ, but its transverse ordering is different between them [2,3,6]. Therefore, the understanding of the form of the interchain interactions will be advanced in the systematic study of the alloy series.

II. Experimental Results

Figure (1) shows the scattering intensity measured in TTF-TCNQ at several temperatures [2]. At the wave numbers q_b=0.295b* and 0.59b* (which is equivalent to 0.41b*), the so-called $2k_F$- and $4k_F$-anomalies due to the $2k_F$- and the $4k_F$-CDW are observed. The large fluctuation of the low dimension makes the CDW one-dimensional (i.e. q_a and q_c arbitrary) above the Peierls transition temperature 53K. Below 53K (49K in the case of the $4k_F$-CDW), the CDW condenses and forms three-

dimensional structures. The satellite reflection spots are observed [1,2,6]. Figure (2) shows the x-ray data obtained in TSeF-TCNQ [4]. It is to be noted that only the $2k_F$-CDW can be observed. The $2k_F$-CDW is quasi one-dimensional above the transition temperature 29K (but it has short-range order along the transverse directions) and has three-dimensional long-range order below 29K [3,4,5]. The x-ray data obtained in $TTF_{0.4}TSeF_{0.6}$-TCNQ are shown in Fig. (3) [3]. Both the $2k_F$- and the $4k_F$-CDW are present. It was verified that the $2k_F$-CDW has a three-dimensional order (although it is short-range) below the transition temperature ~43K, but the $4k_F$-CDW is one-dimensional at all temperature [1]. Similar results were obtained in $TTF_{0.97}$-$TSeF_{0.03}$-TCNQ [8]. Figure (4) shows the phase diagram of CDW of the alloy series obtained in the x-ray scattering study. The curve of

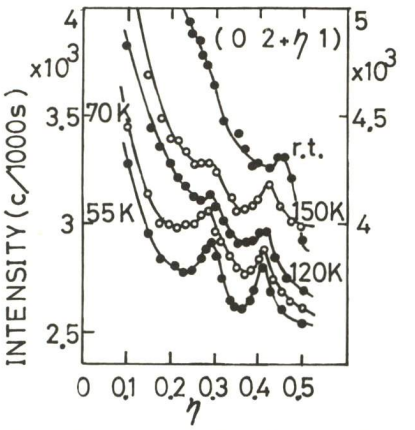

Fig.1 X-ray scattering intensity measured in (021) zone of TTF-TCNQ

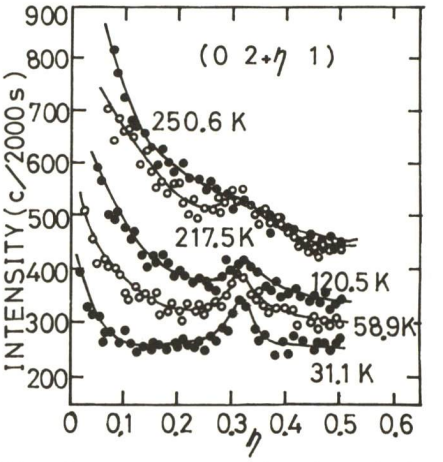

Fig.2 X-ray scattering intensity measured in (021) zone of TSeF-TCNQ

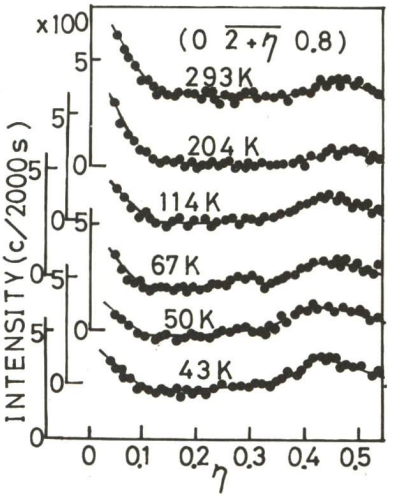

Fig.3 X-ray scattering intensity measured in (021) zone of $TTF_{0.4}TSeF_{0.6}$-TCNQ

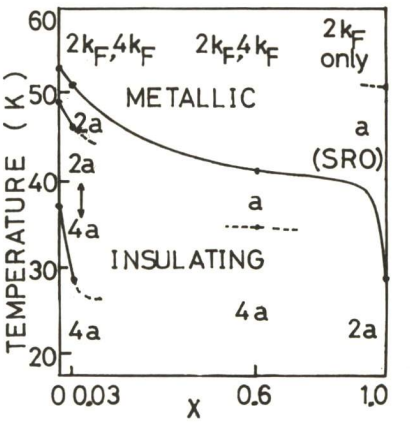

Fig.4 Phase diagram of the CDW in $TTF_{1-x}TSeF_x$-TCNQ

the metal-insulator transition temperature was obtained in transport studies [9].

III. Discussions

We obtain the following conclusions about the properties of the $2k_F$- and the $4k_F$-CDW: The $2k_F$-CDW due to the Peierls mechanism is present predominantly on the TCNQ stack and the $4k_F$-CDW is localed predominantly on the TTF stack. In TSeF-TCNQ, both the TSeF and the TCNQ stack have the $2k_F$-CDW. The origin of the $4k_F$-CDW is presumably the strong intrachain Coulomb interaction among the carriers on the fulvalene stack. One of the possible models is the Wigner crystallization of the localized carriers [10,11].

The reasons are as follows: 1) The correlation lengths shown in Table indicate that the $4k_F$-CDW is more sensitive to the disorder

Table Correlation lengths of the CDW and the relative intensities of the $2k_F$ reflection and the $4k_F$ anomaly in $TTF_{1-x}TSeF_x$-TCNQ

	$2k_F$, 22K			$4k_F$, 20K		
x	ξ_a	ξ_b	ξ_c	ξ_b	$I_{2kF}(20K)$	$I_{4kF}(T>T_P)$
0	>15a	>40b	>30c	>40b	1	1
0.03	4.5a	12b	4.5c	(5-6)b	0.3	4
0.6	4.5a	11b	5.5c	2.3b	0.25	6

introduced in the fulvalene stack than the $2k_F$-CDW. In fact the $4k_F$-CDW has no three-dimensional order in $TTF_{0.97}TSeF_{0.03}$-TCNQ and $TTF_{0.4}TSeF_{0.6}$-TCNQ although the $2k_F$-CDW has the three-dimensional order even in the highly disordered material $TTF_{0.4}TSeF_{0.6}$-TCNQ. 2) As shown in Table, the intensity of the $2k_F$ reflection decreases with increasing TSeF content, but the $4k_F$ increases. This fact suggests again that the $2k_F$-CDW is located on the TCNQ stack and the $4k_F$ on the fulvalene stack because the Se-atoms introduced into the fulvalene stack are the stronger x-ray scatterers than the S-atoms. 3) With regard to the origin of the $4k_F$-CDW, it is to be noted that a ratio U/4t (U; intrachain Coulomb interaction among carriers, 4t; the band width) is larger on TTF stack than on the TCNQ and TSeF stacks. The thermoelectric power in the metallic phase is negative in TTF-TCNQ and is positive (and small) in TSeF-TCNQ [12,13]. This fact indicates that the band width of TTF stack may be smaller than those of TCNQ and TSeF stacks; $4t_{TTF} < 4t_{TCNQ} < 4t_{TSeF}$. Band calculations have suggested the validity of this inequality [14]. Although the relative magnitudes of U are not clear among TTF, TCNQ and TSeF stacks, it is not unreasonable to expect that $U_{TSeF} < U_{TTF}$. When U/4t is larger on TTF stack, the carriers will tend to localize and the $4k_F$-CDW is expected to develop. On the TSeF stack, the $2k_F$-CDW, instead of the $4k_F$, is expected to appear since U/4t will be comparable to or smaller than that of the TCNQ stack.

The three-dimensional ordering of the $2k_F$-CDW has been understood in terms of the Ginzburg-Landau model for the interchain interaction among CDW:

$$F = U_{QQ}\phi_Q\phi_Q^* + U_{QF}\phi_Q\phi_F^* + U_{FF}\phi_F\phi_F^* + W_{QF}\phi_Q^2\phi_F^{*2} + \ldots + c.c. \quad (1)$$

Here ϕ_α denotes the order parameter of the CDW on the α-stack. In TTF-TCNQ, the transverse periodicity along the a-axis is explained by the first and the second terms and their competition [15]. The 4a-state at the lowest temperature range is thought to be due to a

commensurability energy term [15]. In the case of TSeF-TCNQ, which will have the $2k_F$-CDW on both the TSeF and the TCNQ stacks, the second term is expected to dominate because the interchain distance between neighbouring TSeF and TCNQ stacks is shorter than others, and the a-state in the metallic phase can be explained [4]. The 2a-state below 29K may be explained by the dominance of the fourth order term which can become larger than the second order terms when the CDW grows [4,16]. The transverse order of $TTF_{0.97}TSeF_{0.03}$-TCNQ is thought to be of the similar origin to that in TTF-TCNQ. However, the state in $TTF_{0.4}TSeF_{0.6}$-TCNQ is different from those of TTF-TCNQ and TSeF-TCNQ. The a-state just below the transition temperature may be due to the second term as was the case in the metallic phase of TSeF-TCNQ. A reason for the absence of the 2a-state in $TTF_{0.4}TSeF_{0.6}$-TCNQ will be that the growth of the $2k_F$-CDW is suppressed on the fulvalene stack because of the randomness.

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