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Pressure- and Anion-Dependences of the SDW Phase Transition in the Bechgaard Salts

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The two-dimensional Hubbard model approximating the Bechgaard salts is refined by introducing the second harmonics in the $\boldsymbol{b}\cdot\boldsymbol{k}$ dependence which enable to better reproduce the $\boldsymbol{k}$-dependence of the one electron energy near the Fermi surface. The nesting-breaking component among the second harmonics is found to contribute a new term as important as the known one to the stability criterion of SDW. New transfer energy data reveal that this term is prominently enhanced at low temperatures and further with increased pressure, which clarifies the properties of the title in the light of the modified criterion.

The total energy of the SDW state under magnetic field at absolute zero temperature was recently calculated on the basis of the the two-dimensional (2D) tight-binding band Hubbard model with account of the effect of the field to the orbital motion.[1] This calculation enabled to obtain the subphases in the magnetic-field-induced SDW (FI-SDW) phase specified by the occupancy of the quantized closed orbits and to well understand the anomalous oscillatory field dependences of the magnetotransport coefficients[2] and the magnetization.[3]

But the energy gain under field obtained from the magnetization data is larger than the calculated by a factor of 3 with reasonable parameter values. This suggests that the energy range around the SDW gap where the semiclassical closed orbits are formed under the field perpendicular to the 2D plane is more extended, i.e., the Fermi surface nesting is more deteriorated than expected from the simplified model. Therefore we went one step further in better approximating the actual $\boldsymbol{k}$-dependence of the band in the vicinity of the Fermi surface by adding higher harmonic terms proportional to $\cos(2\boldsymbol{b}\cdot\boldsymbol{k})$ and $\sin(2\boldsymbol{b}\cdot\boldsymbol{k})$ to the model band energy, since they were known to deteriorate the Fermi surface nesting.[4] One of two components proved to contribute a new term as important as the already known one to the width of the closed orbit regions and at the same time to the inequality required for the stability of the SDW having the optimal wave vector.[5]

Recently Gallois *et al.*[6] succeeded in obtaining not only the atomic positions at low temperatures for $(TMTSF)_2PF_6$ and $(TMTSF)_2ClO_4$ but also those at 1.7 K and under pressure of 7 kbar for $(TMTSF)_2PF_6$. With the new positional data Ducasse *et al.*[7] calculated the transfer energies. These values reveal that the above-mentioned new term is remarkably enhanced not only with decreasing temperature but with increasing pressure, clarifying the properties of the title in the light of the modified inequality.

Ducasse *et al.*[7] define the symbols for the transfer energies as in Fig. 1. Their results are given in the left part of Table I. The results of Grant[8] are added for comparison. The band energy ε_k for the wave vector $\boldsymbol{k}$ is given by

$$\varepsilon_k = 2t_{I3}\cos y + 2t_{I4}\cos(2x-y) \pm |t_{S1}\exp(\mathrm{i}2x) + t_{S2} + t_{I1}\exp(\mathrm{i}(2x-y)) + t_{I2}\exp(\mathrm{i}y)|, \quad (1)$$

where $x=\boldsymbol{a}\cdot\boldsymbol{k}/2$ and $y=\boldsymbol{b}\cdot\boldsymbol{k}$ with $\boldsymbol{a}$ and $\boldsymbol{b}$ being the unit lattice vectors. From here on we use only the upper branch of eq. (1), since the holes occupying the latter branch makes the SDW of our interest. Expanding in powers of small parameters and compiling the y-dependent terms, we get

$$\varepsilon_k=2t_a\cos x+2q(x)\cos[y-\phi(x)]-[(\Delta t_T)^2/2t_a\cos x]\cdot\cos 2(x-y), \tag{2}$$

where

$$t_a=(t_{S1}+t_{S2})/2,\quad t_T=(t_{I1}+t_{I2})/2,\quad \Delta t_T=(t_{I1}-t_{I2})/2,$$
$$q(x)=[(t_{I3}+t_{I4}\cos 2x+t_T\cos x)^2+(t_{I4}\sin 2x+t_T\sin x)^2]^{1/2}, \tag{3}$$
$$\phi(x)=\tan^{-1}[(t_{I4}\sin 2x+t_T\sin x)/(t_{I3}+t_{I4}\cos 2x+t_T\cos x)]. \tag{4}$$

Since the $\boldsymbol{k}$-dependence in the vicinity of the Fermi surface gives the dominant contribution to physical properties, we can approximate the second and third terms in eq. (2) by fixing the x-argument at $\pm x_F=\pm\pi/4$ in view of the positions of the two pieces of the Fermi surface in the Bechgaard salts in which there is one hole per two TMTSF molecules. We can further refine the model of one electron energy by better reproducing the $\boldsymbol{k}$-dependence of ε_k in the vicinity of the Fermi surface; by putting the refined position $x\simeq\pm(x_F+t_b\cos\eta/t_a\sin x_F)$ of the Fermi surface into the x-argument of eq. (2), we obtain as our model

$$\varepsilon_k=2t_a\cos x+2t_b\cos\eta+2\tau_{\cos}\cos 2\eta\pm 2\tau_{\sin}\sin 2\eta, \tag{5}$$

where the double sign is for $x\gtrless 0$, $t_b=q(x_F)$, $\phi=\phi(x_F)$, $\eta=y\mp\phi$,

$$\tau_{\cos}=-[t_T(t_{I3}+t_{I4})\sin x_F+2t_{I3}t_{I4}]/2t_a\sin x_F-[(\Delta t_T)^2/4t_a\cos x_F]\cdot\sin 2\phi, \tag{6}$$
$$\tau_{\sin}=[t_T^2+2t_{I4}^2+t_T(t_{I3}\cos x_F+3t_{I4}\sin x_F)]/2t_a\sin x_F-[(\Delta t_T)^2/4t_a\cos x_F]\cdot\cos 2\phi. \tag{7}$$

We used $\cos 2x_F=0$ and dropped constant terms. The values of the parameters in eq. (5) are evaluated in the right part of Table I by using the data in its left part. The first terms in eqs. (6) and (7) are given rise since the x-and y-dependences cannot be separated rigorously into two terms due to the existence of plural transverse transfer energies. The second terms come from the dimerization of the TMTSF columns. The actual transfer energies between two molecules separated by $2\boldsymbol{b}$ are diminished by a factor of order $10^{-(5\sim6)}$ than t_b and neglected here.[8] Gor'kov *et al.* first introduced the $\cos 2\boldsymbol{b}\cdot\boldsymbol{k}$ term in ε_k as the nesting-breaking term without specifying its origin.[4]

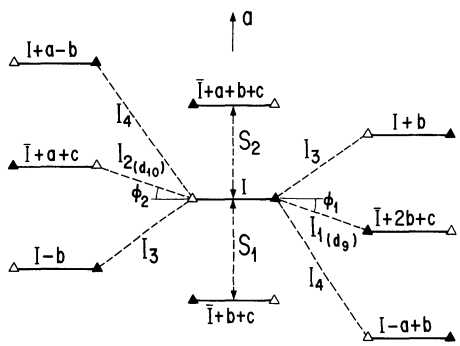

Fig. 1. Schematic figure defining the symbols for the transfer energies donoted by dashed lines. It also defines the angles ϕ_1 and ϕ_2 and the Se-Se contacts d_9 and d_{10}. (After ref. 6)

From now on we assume $\boldsymbol{a}$ and $\boldsymbol{b}$ perpendicular to each other without loss of generality. Without the third term proprotional to $\cos 2\eta$ in eq. (5), the two pieces of the Fermi surface well nest each other with the optimal wave vector

$$\boldsymbol{Q}_0=(2k_F,\ (\pi+2\phi)/b). \tag{8}$$

Due to the finite value of the second derivative of the first term with respect to k_x at the Fermi surface, i.e., at $k_x=\pm k_F$, the complete nesting is broken and the extremum curves giving the bottom and the top of the upper and lower bands, respectively, plotted as functions of k_y are undulated with amplitude[5]

$$\varepsilon_0=t_b^2\cos x_F/2t_a\sin^2 x_F. \tag{9}$$

When we take account of the third and fourth terms in eq. (5), the Fermi surface nesting is further deteriorated, although the optimal wave vector is still given by eq. (8). The extremum curves are obtained via the procedure as in ref. 5. In the leading term approximation, with assumption $\tau_{\cos}\sim\tau_{\sin}\sim t_b/10\sim t_a/100$, they are given by

$$E_\pm=(\varepsilon_0-2\tau_{\cos})\cos 2\eta\pm M_0+\text{const}, \tag{10}$$

Table I. Values of the band parameters in the refined one electron energy model, eq. (5), for $(TMTSF)_2X$ and $(TMTTF)_2X$. They were obtained from the results of the transfer energy calculations by Ducasse *et al.*[7] and Grant[8] shown in the left part of the Table. The symbols for the transfer energies are defined in Fig. 1. The unit of energy is meV.

Compound	Temp.	Press.	Ref.	t_{s1}	t_{s2}	t_{t1}	t_{t2}	t_{t3}	t_{t4}	t_a	t_b	ϕ	ε_0	$\tau_{\cos}$	$\tau_{\sin}$
$(TMTSF)_2PF_6$	300 K	1 bar	7	252	209	−6.4	−13.3	40.2	2.7	231	33.5	−7.3	3.44	0.26	−0.71
$(TMTSF)_2PF_6$	4 K	1 bar	7	280	254	−17.8	−47.9	46.9	5.6	267	29.5	−36.7	2.31	2.13	−0.98
$(TMTSF)_2PF_6$	1.7 K	7 kbar	7	290	272	−20.6	−53.5	49.8	6.2	281	30.9	−40.3	2.41	2.47	−0.92
$(TMTSF)_2ClO_4$	300 K	1 bar	7	258	221	−11.6	−28.3	41.2	3.6	240	29.1	−21.2	2.49	1.06	−0.99
$(TMTSF)_2ClO_4$	7 K	1 bar	7	287	266	−34.0	−64.1	46.2	7.5	277	29.5	−67.0	2.23	3.20	0.55
$(TMTTF)_2PF_6$	300 K	1 bar	7	137	93	1.3	0.0	12.3	0.7	115	12.8	5.2	1.01	−0.14	0.05
$(TMTTF)_2PF_6$	4 K	1 bar	7	146	123	−4.8	−10.6	16.9	1.3	135	12.2	−19.9	0.78	0.30	−0.28
$(TMTTF)_2Br$	300 K	1 bar	7	133	119	−7.8	−9.5	17.2	1.2	126	12.1	−23.9	0.83	0.40	−0.28
$(TMTSF)_2PF_6$	300 K	1 bar	8	395	334	−9.5	−36.2	41.5	9.9	365	26.1	−13.9	1.32	0.10	−0.99
$(TMTSF)_2ClO_4$	300 K	1 bar	8	393	339	−15.3	−54.4	45.1	11.5	366	24.3	−32.7	1.14	1.03	−1.09
$(TMTTF)_2Br$	300 K	1 bar	8	256	223	−12.8	−36.7	26.9	8.8	240	12.8	−42.8	0.48	0.66	−0.50

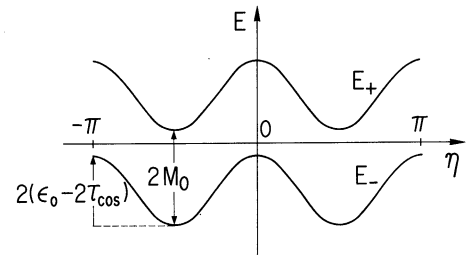

Fig. 2. Schematic figure of the extremum curves giving $E_{\pm}$ as functions of $\eta=bk_y-\phi$ in eq. (10). The origin of the ordinate is arbitrary.

and illustrated in Fig. 2; M_0 is the gap parameter at absolute zero. Therefore the energy range of the closed orbit regions, where the semiclassical closed orbits[9] are formed under the magnetic field parallel to the c^*-direction and which are the hollow parts of the extremum curves in Fig. 2, is changed from $2\varepsilon_0$ to $2|\varepsilon_0-2\tau_{\cos}|$. The criterion for no overlap of the two bands on the both sides of the SDW gap is modified to

$$|\varepsilon_0-2\tau_{\cos}|<M_0. \tag{11}$$

From eq. (6) $\tau_{\cos}$ has the same order of magnitude as $\varepsilon_0\sim t_b^2/t_a$. We have carried out our calculation keeping the accuracy of this order.

When the inequality (11) is held, the gap equation can be solved with the result $M_0\simeq(4t_a\sin^2 x_F/\cos x_F)\cdot\exp[-1/IN(0)]$, where $N(0)=N_s/4\pi t_a\sin x_F$ is the state density per spin per one k_x-branch with the site density N_s. When (11) is violated, the electron and hole pockets arising due to band overlap give very strong negative contributions, as was seen in ref. 5 and so the gap parameter vanishes or is diminished quickly to zero as we go away from the parameter region satisfying (11). Therefore this inequality determines in the first approximation the stable parameter region of SDW.

The numerical data obtained for $(TMTSF)_2X$ with $X=PF_6$ and ClO_4 in Table I show that $\tau_{\cos}$ is remarkably enhanced at low temperatures, exceeding ε_0 which is weakly temperature dependent. Further in the case of $(TMTSF)_2PF_6$ $\tau_{\cos}$ is sharply increased in contrast to slight increase of ε_0 under pressure of 7 kbar. Since the inequality (11) is considered to be held at ambient pressure and violated

under pressure of 7 kbar where SDW does not appear in the absence of field, we have to conclude that in the case of the PF_6 salt $2\tau_{cos}$ is larger than ε_0 already at ambient pressure at low temperatures, satisfying (11), and that (11) is violated due to the increase of τ_{cos} and not of ε_0. The possibility that M_0 is appreciably diminished under pressure due to weakening of the Umklapp process is excluded later.

This situation necessitates the value of $M_0 \simeq |\varepsilon_0 - 2\tau_{cos}| = 2.5$ meV around the critical pressure close to 7 kbar where SDW disappears at absolute zero. Then from Table I and the value of the indirect gap, we get the value of the activation energy $E_A = M_0 - |M_0 - 2\tau_{cos}| = 0.6$ meV at ambient pressure, if the value of M_0 is not much changed by the change of pressure by about 7 kbar. The value $M_0 = 20.5\ k_B = 1.8$ meV given by the mean field relation from the transition temperature $T_{SDW} = 11.5$ K is considered slightly too small due to the neglect of the fluctuation effects. The most plausible value for the PF_6 salt is estimated at $33\ k_B = 2.8$ meV from the thermoreflectance gap[10] if we interpret it as the direct gap. The theory of the energy gain of the FI-SDW state under field also supports the similar magnitude of M_0. The saturation value of this energy was found[11] to be proportional to the square of the energy range of the closed orbit region, therefore to the square of $2|\varepsilon_0 - 2\tau_{cos}| \sim 2M_0$. The discrepancy of factor 3 mentioned earlier leads to $M_0 \sim 35\ k_B = 3.0$ meV, although for the ClO_4 salt. The above necessitated value of 2.5 meV is in good agreement with 2.8 meV. The value of E_A at ambient pressure is known to be $24\ k_B = 2.1$ meV,[12] which is three times the above mentioned value 0.6 meV but not in disagreement in view of the accuracy of the band parameter calculation. General idea on accuracy of the latter can be got by comparison with the experimentally obtained values of t_a and t_b.[13]

If the Umklapp process works, M_0 should be diminished under pressure.[14] But it needs as the prerequisite the commensurability of the wave vector $\boldsymbol{Q}_0$, eq. (8), which has been known theoretically accidental.[5a] And recent NMR analyses strongly deny it; Delrieu *et al.*[15] showed that the SDW wave vector in $(TMTSF)_2PF_6$ is $\boldsymbol{Q} = (a^*/2, (0.2 \pm 0.05)b^*, ?)$, which is not commensurate at least with a small integer. Takahashi *et al.*[16] reported that their NMR data were best fitted with an incommensurate value of Q_b close to $0.25b^*$. The Q_b value expected from eq. (8) and the band parameter in Table I is $Q_b = 0.30b^*$, which is in fair agreement with the observed.

The results in Table I for the average structure of relaxed $(TMTSF)_2ClO_4$ at 7 K reveal that the inequality (11) is violated already at ambient pressure, since the value of $|\varepsilon_0 - 2\tau_{cos}| = 4.2$ meV amply exceeds the plausible value of M_0. The band modification due to the anion ordering deteriorates further the Fermi surface nesting.[17] The appearance of SDW in the quenched $(TMTSF)_2ClO_4$ sample suggests that the inequality is held with a much smaller value of τ_{cos}. This state disappears under pressure between 2 and 3 kbar.[18] Since the activation energy in the SDW state is estimated at $6\ k_B \simeq 0.5$ meV from the data in ref. 19, the indirect gap of this salt shrinks with almost the same rate under pressure as $(TMTSF)_2PF_6$. Therefore the mechanism of disappearance of SDW in both salts must be the same. Then if the Umklapp process works, it must be working in the both sytems, which is considered too accidental.

Since t_{I1} and t_{I2} are the most sensitive to the pressure of the transfer energies as seen in Table I, the tendency of ε_0 and $2\tau_{cos}$ under pressure can be seen from their derivatives with respect to $t_T = (t_{I1} + t_{I2})/2$ as follow:

$$\partial\varepsilon_0/\partial t_T = (t_{I3} + t_{I4})/t_a + \sqrt{2}\, t_T/t_a, \tag{12}$$

$$\partial(2\tau_{cos})/\partial t_T = -(t_{T3} + t_{I4})/t_a. \tag{13}$$

The righthand side of eq. (12) is almost cancelled and much weaker than the righthand side of eq. (13). Since the crystallographic work verified[6c] that the angles ϕ_1 and ϕ_2 in Fig. 1 remain almost constant under pressure at low temperatures, against expectation for increase, with only the Se-Se contact lengths d_9 and d_{10} contracted, surely t_T must keep its negative sign and increase its absolute magnitude under pressure from the nature of the π-orbital of the present interest. And the enhanced deviation from the simplified band model due to the increased t_T necessitated the present refinement, which is considered to take account of the large temperature- and pressure-

dependences of t_{l1} and t_{l2} in an essential way.

Concerning the contribution of the transfer energies in the c-direction, a similar argument leads to the contribution of order t_c^2/t_a to the undulation amplitude of the extremum curves as functions of k_c in the case of the optimal wave vector. But it is estimated at the order of 0.1 meV and negligible.

The introduction of $\tau_{\cos}$ allows to extend the closed orbit regions, leading to the increased energy gain of the FI-SDW state. It can also change the period of the transitions among subphases. In the absence of the field we can substantiate now more appropriately the idea[20] of the first-order transition boundary between the SDW state and the reentrant region in the PT-phase diagram of the PF_6 and AsF_6 salts. In doing so, we have to keep in mind that even with finite $\tau_{\cos}$ there is around the parameter region defined by the inequality (11) the peripheral transient region, found previously[21] with $\tau_{\cos}=0$, where the SDW wave vector is gradually shifted from $\boldsymbol{Q}_0$ and that M_0 is diminished, finally to zero, as the parameter set goes away from the region of the stable SDW defined by (11).

In summary, we have refined the one electron energy in the 2D Hubbard model better reproducing the 2D tight-binding band of the Bechgaard salts in the vicinity of the Fermi surface by introducing the second harmonic components of the $\boldsymbol{b}\cdot\boldsymbol{k}$ dependence to the previous simplified energy model. The coefficient of the nesting-breaking component among them was found to add an important term of the same order as the known one to the criterion for the stability of SDW having the optimal wave vector. From new transfer energy data it proved to be increased prominently at low temperatures and further with increased pressure and so enabled to well understand the pressure- and anion-dependences of the SDW transition according to the modified criterion.

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