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THEORY OF THE PHASE DIAGRAM OF THE $(TMTSF)_2X$ SALTS

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Abstract The theory of the title is developed on the SDW phase and the reentrant superconducting region on the basis of 2D tight-binding band model. Quantization of closed orbits is shown to lead to the magnetic-field induced SDW.

INTRODUCTION

Most people studying the Bechgaard salts $(TMTSF)_2X$ (X=PF_6, AsF_6, ClO_4 etc.) agreed[1-5] that the ratio of transfer energies t_a and t_b along the a- and b-axis directions, respectively, is around 10 and that t_c is smaller than t_b by more than one order. But only few authors[3,6,7] asserted that this unexpectedly large value of t_b destroys SDW and makes superconductivity appear. This two-dimensional (2D) picture was opposed by the 1D viewpoint,[8] which claims that SDW vanishes since the Umklapp process is weakened. The first half of this presentation sketches our main results on the phase diagram on the basis of the 2D band model and experimental evidences strongly supporting this scheme. The second half aims at clarifying the puzzle of the magnetic-field induced SDW (FI-SDW). On the basis of the present model semiclassical quantization of the orbital motion under the field is shown to actually lower the energy of the SDW state, leading to FI-SDW.

SDW OF THE ANISOTROPIC 2D HUBBARD MODEL

The electronic band of the Bechgaard salts can be reduced to[3d]

$$\varepsilon_{\underline{k}} = -2t_a \cos \underline{a}\cdot\underline{k} - 2t_b \cos(\underline{b}\cdot\underline{k} \mp \theta), \quad \text{for } \underline{a}\cdot\underline{k} \gtrless 0, \qquad (1)$$

where $\underline{a}$ is the half of the actual unit vector in the stacking direction; $\underline{b}$ is the transverse unit vector parallel to the TMTSF sheet. t_b and θ depend on the transfer energies between neighboring molecules and $\underline{a}\cdot\underline{k}$, but when $t_a >> t_b$, as is the case, they can be considered as constants having the values defined around the Fermi surface. If we use the values of transfer energies obtained by Grant,[4] the value of θ for the Bechgaard salts is estimated at around -20°. This is too large for the commensurate SDW to be realized, which is the prerequisite for the Umklapp process to work. Since except for it the phase θ plays no role, we assume $\theta=0$ in the following. Making electron-hole reversal, we assume 0.5 electron per molecule, which gives the Fermi wave vector $k_F=\pi/4a$.

In spite of the warping due to the finite value of t_b, the two pieces of the Fermi surface well nest[9] with the nesting nector $\underline{Q}_o=(2k_F, \pi/b)$, which is called optimal wave vector. With the aid of this 1D-like feature, the Coulomb interaction between electrons drives SDW. For simplicity we employ as our model system the Hubbard Hamiltonian defined by the interaction constant I and the one-electron energy given by eq. (1). SDW makes the gap, the magnitude of which we denote by 2M, around the position where the Fermi surface is situated in the normal state. This position of the SDW gap is sinusoidally shifted around k_F, in the k_x-coordinate depending on k_y. Also the levels of the top of the lower band and of the bottom of the upper band on the both sides of the gap have a weak dependence on k_y, as shown in Fig. 1a. The amplitude of this undulation is given by[3a]

$$\varepsilon_o = t_b^2 \cos x_F / 2t_a \sin^2 x_F, \quad x_F = ak_F \ . \tag{2}$$

When $\varepsilon_o < M_o$ at temperature T=0 K, M_o being M at T=0 K, the upper and lower band do not overlap. Then the gap equation has the solution $M_o=4t_a \sin^2 x_F/\cos x_F \cdot \exp(-1/N(0)I)$, where $N(0)=N_{site}/4\pi t_a \sin x_F$ is the state density. This is the same as the solution of the 1D system. But when $\varepsilon_o > M_o$, carrier pockets appearing due

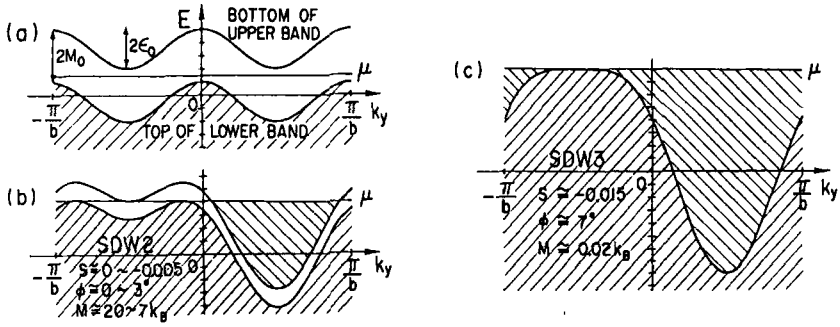

FIGURE 1 Extremum curves of upper and lower bands in the case of (a) the usual SDW, (b) SDW2 and (c) SDW3. Hatched parts are occupied by electrons.

to the overlap between the upper and lower bands make such a big negative contribution to the gap equation that we have no more a solution which can be continuated to the one for $\varepsilon_o < M_o$. It is interesting to note that the difference[3b] of the ground state energy between the SDW and normal state is $N(0)(\varepsilon_o^2 - M_o^2)$. Therefore, we get the condition $\varepsilon_o < M_o$ or an upper bound $t_{b,cr}$ of t_b for the existence of SDW. $t_{b,cr}$ is given by[3d]

$$t_{b,cr} = (3.53\, T_{SDW}^{(o)}\, t_a \sin^2 x_F / \cos x_F)^{1/2}, \qquad (3)$$

where $T_{SDW}^{(o)}$ is the mean field SDW transition temperature T_{SDW} in the limit of $t_b = 0$. This upper bound is similar to that to the transverse coupling for the 3D-coupled quasi-1D Peierls system.[9] T_{SDW} was numerically calculated and shown in Fig. 2a.

Gor'kov et al.[10a] and Héritier at al.[10b] used for convenience of treatment a term $\propto \cos 2bk_y$ as destroying Fermi surface nesting. But the direct transfer energy giving this term is negligible. A similar term resulting from dimerization gives a contribution smaller by one order to the undulation of the band extrema.

The most precise values of t_b and t_a, therefore $t_{b,cr}$, can be obtained from the plasma frequency data[5] as in Table I. Closeness of t_b and $t_{b,cr}$ is amazing and strongly supports our claim that SDW

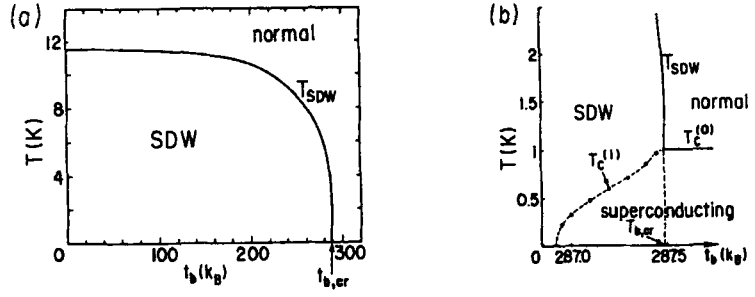

FIGURE 2 (a) Curve of T_{SDW} vs t_b and (b) first-order transition temperature $T_c^{(1)}$ between the SC and SDW phases as a function of t_b. t_a = 250 meV and $T_{SDW}^{(o)}$ = 11.5 K were assumed.

vanishes, under pressure or depending on the features of the anion, because t_b exceeds $t_{b,cr}$ or ε_o exceeds M_o. ε_o has tendency to increase under pressure and M_o to decrease. The steep descent of T_{SDW} in the TP-phase diagram[11a] at the approach of pressure P to its critical value can be well understood from the fact that T_{SDW} falls as ε_o approaches M_o, or more simply as t_b approaches $t_{b,cr}$ as in Fig. 2a if we take account of the increase of t_b under pressure. t_b is composed of interstack intermolecular transfer energies.[3d] The one between the molecules of the interstack closest contact has the opposite sign to the others, giving a negative contribution to t_b.[4] It tends to change sign[3d] when the angle between the closest Se-Se contact and the molecular plane increases, which is plausible to occur under pressure.

The reentrant region in the PT-phase diagram[11a] was found the purely superconducting (SC) phase, which replaces the SDW phase simply because its free energy is lower.[3b] Therefore the boundary

X	t_a(meV)	t_b(meV)	$t_{b,cr}$(meV)
ClO_4	265	26.0	25.6
PF_6	245	22.8	24.6
AsF_6	287	22.4	26.7

TABLE I Values of t_a, t_b and $t_{b,cr}$ of $(TMTSF)_2X$. The data[5] of plasma frequencies $\omega_{pl,i}$ were analyzed by means of their expressions taking account of obliqueness between a and b and of the correction from t_b to $\omega_{pl,a}$. Structural data came from Ref.7 of Ref.4.

between them must be of the first-order. This nature was recently observed by Azevedo et al.[12a] The phase boundary $T_c^{(1)}$ in Fig. 2b which was obtained by adding a BCS-type interaction to our Hubbard model has nice features. Solutions allowing coexistence of both orders were looked for but only an unstable one was found.[3b]

SDW WITH SHIFTED WAVE VECTOR AND FIELD-INDUCED SDW

Shubnikov-de Haas (SdH)-like oscillation of the magneto-resistance,[2b,13,14,11b] NMR[15] and ESR[12b] studies and Hall voltage experiments[16] have established that the magnetic field parallel to the c*-axis induces, from the normal state, SDW states (FI-SDW) with carrier pockets of $0.3 \sim 1\%$ of the Brillouin zone. This size of carrier pockets can exist only when the SDW wave vector is shifted from the optimal one $\underline{Q}_o$. In this second part, we see that such a shift, slight but enough, is energetically possible around the precedingly obtained phase boundary even in the absence of field. Then the orbital quantization under field is shown to actually lower the energy of the SDW state, leading to FI-SDW.

The polarization of the SDW magnetization is along the b-axis. The magnetic field H is applied parallel to the c-axis. Then we get the following effective Hamiltonian:

$$H_{eff} = \sum_{\vec{k}\sigma} C^+_{\vec{k}\sigma}[-2t_a\cos ak_x - 2t_b\cos b(k_y - (ieH/c)\cdot\partial/\partial k_x) - \mu_B H\sigma - \mu]C_{\vec{k}\sigma}$$
$$- [\,iM(C^+_{\vec{k}\uparrow} C_{\vec{k}-\vec{Q}\downarrow} + C^+_{\vec{k}-\vec{Q}\uparrow} C_{\vec{k}\downarrow}) + h.c.] \quad , \qquad (4)$$

where we take account of the effect of the field through orbits and also of the Zeeman term. The shifted SDW vector is defined by $\underline{Q}=(2k_F(1+s), (\pi-2\phi)/b)$; s and ϕ define the shift. In terms of the eigenvalues $E_{i\sigma}$ of eq. (4) the energy of the system is given by

$$E_{SDW} = \sum_{\sigma}\sum_{i} (E_{i\sigma} + \mu) f(E_{i\sigma}) + 2M^2/I \qquad (5)$$

as a variational function of M, s and ϕ. Chemical potential μ is

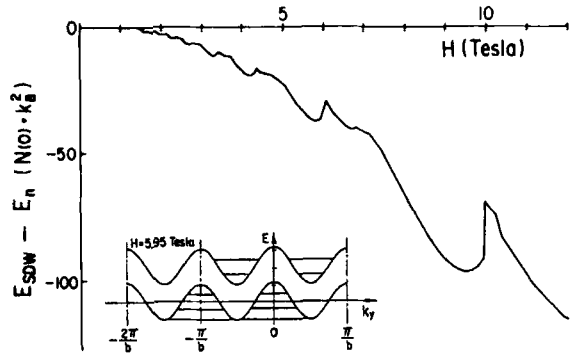

FIGURE 3 E_{SDW}-E_n vs magnetic field H for t_b=326 k_B. The inset shows an example of quantized levels.

always adjusted to keep the electron number constant.

In the case of H=0, after minimization of eq. (5) two new type of SDW appeared as the ground state[3c]; one (SDW2) at $t_b \sim (t_{b,cr} - 1\ k_B,\ t_{b,cr} + 2\ k_B)$ and the other (SDW3) at $t_b \gtrsim t_{b,cr} + 2\ k_B$. Band extremum curves of these states are shown in Figs. 1b and 1c. They have a carrier pocket of order of the observed size. Since M of SDW3 is very small, leading to $T_{SDW3} \sim 0.01$ K, it does not essentially modify the argument on the upper bound of t_b.

When H≠0, H_{eff} is reduced to a matrix of very big size. Instead of solving it, quantum levels were obtained by applying the semiclassical quantization rule[17] to the closed orbits formed in the SDW-reorganized band under the field. The area of the closed orbit in the k-space is equated to $2\pi eH(n + 0.5)/c$. The orbital degeneracy of each quantum level is $N_{site}abeH/2\pi c$. Concerning the part of the k-space where there are only open orbits, we use the same state density as that in the absence of field, since its modification by the field there is minor.

Figure 3 shows E_{SDW} subtracted by the normal state energy E_n as a function of H with fixed parameter values $M=M_o=20.46\ k_B$ and $s=\phi=o$. t_b=326 k_B was chosen since $t_{b,cr} \cong 325.6\ k_B$ in this case with t_a=3690 k_B and $T_{SDW}^{(o)}$=11.5 K. In order to conserve the

number of states the above rule was slightly modified; e.g., when the number of states contained in the quantized levels exceeds that in the closed orbit region, the open orbit region is cut in computing eq. (5) and in the opposite case, another quantized level is added in the open orbit region in noting Ref. 17b. The curve clearly shows that the quantization of orbits decreases E_{SDW} and therefore induces SDW. The decrease corresponds to the susceptibility increase by 40% of the Pauli paramagnetism, which is in good agreement with the observation.[18] This decrease of energy due to the level discretization occurrs since when the $dN(\varepsilon)/d\varepsilon < 0$ in the absence of field, the quantized level is lower than the average energy of all the states which converge to the former under the field and that actually we see $dN(\varepsilon)/d\varepsilon < 0$ in the k-space region of closed orbits in the lower band (see Fig. 5 in Ref. 3a). The curve in Fig. 3 periodically peaks when the lowest quantum levels disappear as the field is increased.

Since Fig. 3 was obtained from the variational function, with fixed variables, we can expect to get a lower energy by adjusting M, s and ϕ and to have several minimum energy curves as a function of H, each of which is supposed to have a definite number of quantum levels in the lower bands. The real minimum is given by the lower envelope of the above-mentioned curves. Therefore, as the field is increased, the system moves jumping from one minimum curve to another. This is considered the transitions observed in the Hall voltage experiment and also in the SdH-like oscillation.

The recent theories of Refs. 10a and b clarified the FI-SDW instability from the normal state side. The present one started independently and is an approach to FI-SDW from T=0 K.

CONCLUSIONS

The mean field theory of SDW based on the 2D band well accounts for the disappearance of SDW in the Bechgaard salts under pressure or depending on the anion and for the first-order nature of the

transition between the reentrant region and the SDW phases. A slight but enough shift of the SDW wave vector occurrs around the boundary of the SDW phase having the usual optimal wave vector. The quantization of closed orbits under the magnetic field lowers the energy of the SDW state and brings in FI-SDW.

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