PHYSICAL REVIEW B VOLUME 60, NUMBER 6 1 AUGUST 1999-II

Electron-positron momentum density in $(TMTSF)_2ClO_4$

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(Received 16 April 1999)

We have measured electron-positron momentum density in $(TMTSF)_2ClO_4$ by the positron two-dimensional angular correlation of annihilation radiation (2D-ACAR) technique. Significant anisotropies are found in the momentum density reflecting the low dimensionality of the material. *Ab initio* plane-wave pseudopotential calculations have been also made to simulate the 2D-ACAR spectra. The calculated 2D-ACAR spectra are in good agreement with the experimental ones. In order to investigate the Fermi-surface structure, we constructed Lock-Crisp-West (LCW) remapped spectra. The resultant spectra show small steps at the expected Fermi-surface position for both the experiment and the calculation. The magnitude of the steps in the experimental LCW spectrum is one third of the calculated one but still one order of magnitude higher than the experimental detection limit. Although we cannot conclude the existence of an ideal Fermi surface due to the finite experimental resolution, we have confirmed, in the experiment, a structure corresponding to the calculated Fermi break. [S0163-1829(99)51330-1]

In recent years, several attempts have been made to study the electronic (especially, Fermi-surface) structure of organic conductors by the positron two-dimensional angular correlation of annihilation radiation (2D-ACAR) technique.[1–4] A 2D-ACAR spectrum corresponds to a two-dimensional projection of the electron-positron momentum density. They successfully extracted anisotropies in the 2D-ACAR spectra but these anisotropies have much more complex structures than the expected Fermi-surface shape. In our previous work,[4,5] we have demonstrated that theoretical calculations based on molecular-orbital description are very useful and necessary in interpreting experimental results. In the present paper, we report 2D-ACAR measurements on bis-tetramethyl-tetraselenofulvalene perchlorate $(TMTSF)_2ClO_4$ $[TMTSF=(CH_3)_4C_6Se_4]$, which is the first ambient-pressure organic superconductor with the transition temperature of 1.2–1.5 K.[6,7] Its lattice parameters at room temperature were reported as $a=7.266$ Å, $b=7.678$ Å, $c=13.275$ Å, $\alpha=84.58°$, $\beta=86.73°$, and $\gamma=70.43°$.[8] The a axis is the axis with the highest electrical conductivity and the TMTSF molecules are stacked along this axis. TMTSF columns are arranged along the b axis. The TMTSF networks in the ab plane are separated by the insulating ClO_4 layers. As a result, high conductivity appears in the ab plane and the conductivity is the lowest along the direction perpendicular to this plane.[9] The Fermi-surface structure calculated theoretically is rather simple (corrugating sheets) showing the quasi-one-dimensional character[10–13] and expected to be mapped in the experimental 2D-ACAR spectrum more easily compared to materials studied previously.[1–4] On the theoretical aspect, we have calculated electron and positron states as well as 2D-ACAR spectra with a newly developed *ab initio* plane-wave pseudopotential calculation code, which has two advantages over the previous molecular-orbital description:[4,5] better accuracy and absence of empirical parameters.

The 2D-ACAR measurements were made at room temperature on a single crystal of 7.0 mm×2.0 mm×0.2 mm with projection axes along $c*$ and a crystallographic axes ($c*$ is one of the reciprocal lattice vectors). About 2×10^8 coincidences were accumulated in histograms with a mesh of 0.1 mrad×0.1 mrad in two weeks. The overall resolution is estimated at 1 mrad in a full width at half maximum (FWHM). 1 mrad corresponds to 0.137036 a.u. (atomic unit) in the momentum space. After the measurements, each 2D-ACAR spectrum was corrected with the measured angular efficiency of the spectrometer and symmetrized according to the crystal symmetry to reduce statistical errors. Smoothing by a two-dimensional Gaussian function with the FWHM of 1 mrad, which corresponds to the experimental resolution, was also made. As a common feature in 2D-ACAR spectra for complex materials containing many electrons in their unit cells, the presently obtained 2D-ACAR spectra show a rather

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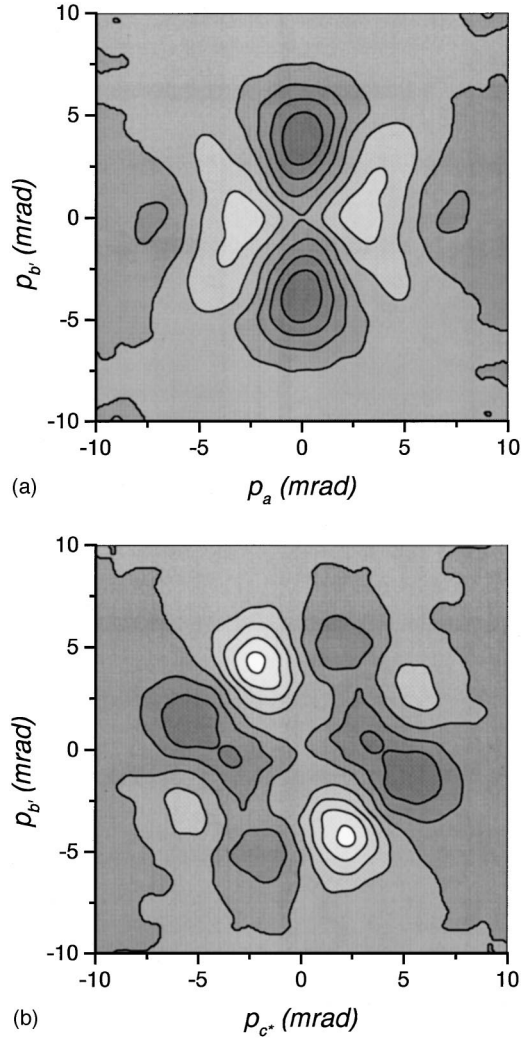

FIG. 1. Experimental 2D-ACAR anisotropy for $(TMTSF)_2ClO_4$, (a) $c*$ projection and (b) a projection. The contours are in steps of (a) 0.2% or (b) 0.1% between (a) $\pm 2\%$ or (b) $\pm 1\%$. The bright parts represent higher values.

structureless bell shape. A useful way to emphasize the differences between 2D-ACAR spectra is to look to the anisotropic parts, which are obtained by subtracting a cylindrical average from the 2D-ACAR spectrum. Figures 1(a) and 1(b) represent experimental 2D-ACAR anisotropies projected along the $c*$ and a axes, respectively. The magnitude of the anisotropies is within $\pm 2\%$ of the signal at the origin $\rho_{2D}(0,0)$ for the former while $\pm 1\%$ for the latter.

The electronic structure of $(TMTSF)_2ClO_4$ has been obtained by *ab initio* plane-wave pseudopotential band calculations[14] with Troullier-Martins type pseudopotentials[15] and the local-density approximation (LDA). We used the Ceperley-Alder correlation[16] parametrized by Perdew and Zunger.[17] Energy cutoff of plane waves were set to 67.5 Ry. 16 $\boldsymbol{k}$ points in the irreducible zone (1/2 of the Brillouin zone) were used. A quasi-one-dimensionality was found as expected. The details of the band calculation have been published elsewhere.[13] The positron wave function was obtained with the same plane-wave basis set, constructing a potential for positrons from the resultant electron wave functions and the electron-positron correlation potential given by Boroński and Nieminen.[18] Once the electron wave functions $\psi_{-j}(\boldsymbol{r})$ (j: band suffix) and the positron wave function $\psi_+(\boldsymbol{r})$ are obtained, the 2D-ACAR spectrum $\rho_{2D}(p_x,p_y)$ (projected along the z direction) can be calculated with the following equations:

$$\rho_{2D}(p_x,p_y)=\int \rho(\boldsymbol{p})dp_z, \tag{1}$$

$$\rho(\boldsymbol{p})=\sum_j \rho_j(\boldsymbol{p}), \tag{2}$$

$$\rho_j(\boldsymbol{p})=\text{const}\cdot\left|\int \psi_{-j}(\boldsymbol{r})\psi_+(\boldsymbol{r})\sqrt{\gamma(\boldsymbol{r})}\exp(-i\boldsymbol{p}\cdot\boldsymbol{r})d\boldsymbol{r}\right|^2, \tag{3}$$

where $\rho(\boldsymbol{p})$ is a three-dimensional electron-positron momentum density and $\rho_j(\boldsymbol{p})$ is a partial momentum density with a band suffix j. $\gamma(\boldsymbol{r})$ is the enhancement factor, describing the enhancement of the electronic density around the positron due to the electron-positron correlation. We used the formula by Boroński and Nieminen.[18] Anisotropies were calculated from the obtained 2D-ACAR spectra, after introducing the experimental resolution. We neglected annihilation with core electrons, whose contribution is estimated to be less than 1%. As for the anisotropy, core contribution should be negligible.

Figures 2(a) and 2(b) represent the calculated 2D-ACAR anisotropies projected along the $c*$ and a axes, respectively. The range is $\pm 5\%$ of $\rho_{2D}(0,0)$. The estimated anisotropies are larger (a factor of 2.5–5) than the experimentally obtained ones. This is a common feature for another complex system, oxide superconductors. Electron correlation effects and/or certain crystalline defects may play roles to smooth out the ACAR structure. In spite of the discrepancy of the magnitude, the overall shapes are in good agreement. This confirms reliabilities of the experiment and the calculation. Since the predicted Fermi surface is corrugating sheets perpendicular to the ab plane, Figs. 1(a) and 2(a) should contain breaks due to the Fermi surface. It is difficult to find such one-dimensional structures in these figures. Strong ''wave-function effects'' seem to screen them out.

The Lock-Crisp-West (LCW) remapping according to the symmetry of the reciprocal-lattice space[19] is sometimes very useful to eliminate ''wave-function effects,'' which do not have the reciprocal-lattice periodicity. In practice, it is accomplished by adding ACAR distributions in higher Brillouin zones to that in the first Brillouin zone. The resultant spectrum corresponds to a projection of the positron-sampled electron occupancy in the momentum space. In Fig. 3(a), the LCW spectrum for the calculation is presented. Again, the original 2D-ACAR was smoothed with the experimental resolution. Only weak ''wave-function effects'' exist as a background, and a significant feature of the one-dimensional Fermi surface appears though the magnitude is rather small: 0.7% in intensity. This small magnitude of the break can be interpreted considering electron and positron distributions. The band crossing the Fermi level is derived from the TMTSF highest-occupied molecular orbital, which is rather localized at the center part of the TMTSF molecule.[13] On the contrary, positrons are distributed around ClO_4 anions since they are negatively charged. As a result, the overlap between these electron and positron wave functions is very small.

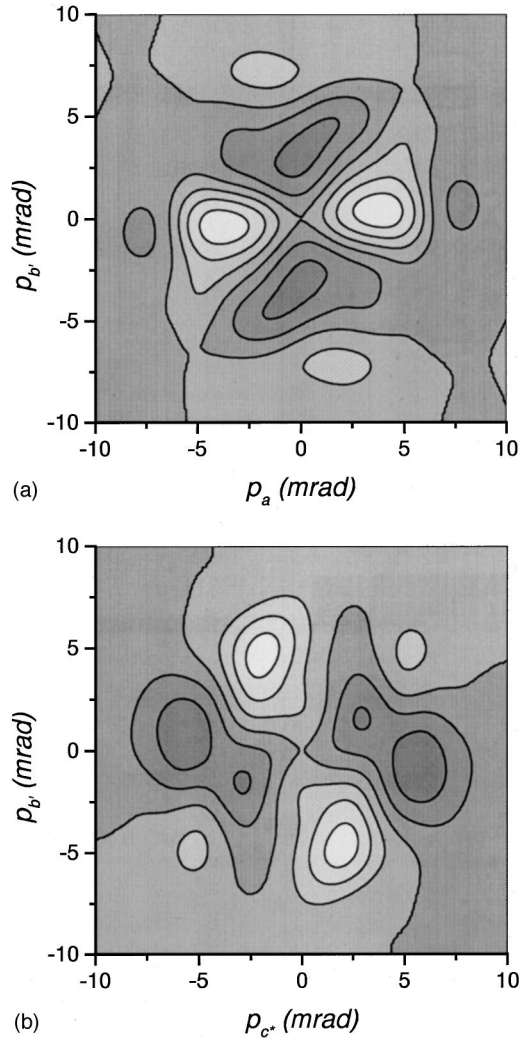

FIG. 2. Calculated 2D-ACAR anisotropy for $(TMTSF)_2ClO_4$, (a) $c*$ projection and (b) a projection. The contours are in steps of 0.5% between $\pm 5\%$. The bright parts represent higher values.

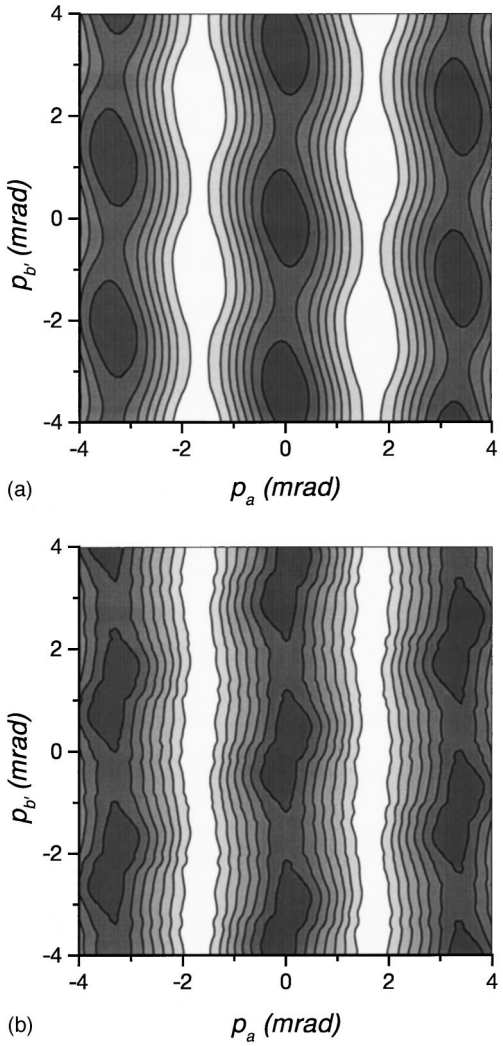

FIG. 3. The LCW remapped spectrum, which corresponds to a projection of positron-sampled electron occupancy in the momentum space, (a) calculation and (b) experiment. Each is shown in the repeated zone scheme. The centers of the darkest area correspond to the projected reciprocal lattice points. The bright parts represent higher values.

Owing to the flat background, such a small break is visible for the present material. Figure 3(b) represents the LCW spectrum for the experiment. One-dimensional features appear again though the magnitude is 0.16%, which is smaller than the above-mentioned theoretical estimation (0.7%), similarly to the anisotropy case. Although it is not easy to estimate the experimental detection limit, the observed break is thought to be one order of magnitude higher than the limit. The observed structure seems significant.

Recently, Zwick *et al.*[20] measured photoemission spectra on $(TMTSF)_2ClO_4$ and reported that neither quasiparticle peaks near the chemical potential nor a Fermi surface was observed. Is what we observed a Fermi surface or not? With the positron 2D-ACAR technique, we can obtain positron-sampled $\boldsymbol{k}$-space occupancy. An ideal Fermi surface obeying the Fermi gas (or liquid) theory should appear as a discontinuity in the occupancy spectrum. With the present experimental conditions, the resolution of ~ 1 mrad, which is too coarse to distinguish a sharp discontinuity, is inevitable. It is, therefore, impossible to confirm the existence of a real Fermi-surface break. Instead, we may conclude that we have found a Fermi-surface-like step in the experimental LCW spectrum, which corresponds well to the calculated result. In this term, the present calculation relying on the Fermi liquid theory is still useful.

In conclusion, we have successfully measured and calculated the 2D-ACAR spectra on $(TMTSF)_2ClO_4$. The overall agreement is very good, and the reliability for the experiment and the calculation has been confirmed. We observed a one-dimensional steplike structure. This steplike structure corresponds to the calculated Fermi break. Due to the finite experimental resolution, it is not possible to distinguish if what we observed is an indication of the ideal Fermi surface obeying the Fermi gas (or liquid) theory or not.

The authors are grateful to Professor Ø. Fischer for his continuous encouragement and to Dr. D. Vasumathi for her help in the experiments. All the calculations were performed at the Research Information Processing System/Station (RIPS) center of the Agency of Industrial Science and Technology (AIST), under the Japanese Ministry of International Trade and Industry (MITI).

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