SHUBNIKOV-DE HAAS EFFECT of α-Et₂Me₂N[Ni(dmit)₂]₂ SALT

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Magnetoresistance of organic conductor, α-Et₂Me₂N[Ni(dmit)₂]₂, was measured for the magnetic field along a* axis up to 23 T in the temperature down to 0.5 K. Three different types of closed orbits (α-, β-, γ-orbit) of two-dimensional Fermi surface were found through Shubnikov-de Haas oscillation. The areas of these three closed orbits are estimated to be 0.23% (α-orbit), 4.60% (β-orbit), and 87.4% (γ-orbit) of the first Brillouin zone. The cyclotron masses for α-, β-, γ-orbit are estimated to be (0.06 ± 0.01)m_e, (0.166 ± 0.011)m_e, (4.3±0.2)m_e, respectively.

I. Introduction

There are a group of conducting charge-transfer salts involving M(dmit)₂ [M=Ni, Pd, Pt], among which seven salts have been found to exhibit superconducting transition at low temperature. One of the interesting features of M(dmit)₂ salts is that not only LUMO but also HOMO of M(dmit)₂ could contribute in the formation of the conduction band because the energy separation between HOMO and LUMO is quite small in M(dmit)₂ molecule. In fact, we found from optical studies that the anti-bonding combination of HOMO of M(dmit)₂ molecules gives an energy level higher than the bonding combination of LUMO's in the cases of the P(dmit)₂ and Pt(dmit)₂ salts which have a strongly dimerized structure. The contribution of HOMO in the formation of the conduction band is expected to vary depending on the degree of dimerization in the crystal structure. This seems to give very characteristic aspect in the electronic structures of M(dmit)₂ salts. Thus it is of great interest to investigate the details of the band structure on this series of charge-transfer salts.

We previously reported the observation of Shubnikov-de Haas effect in α-Et₂Me₂N[Ni(dmit)₂]₂ which has a weakly dimerized structure and is known to be metallic down to 1.3 K without showing superconducting transition. From the analysis of the observed SdH effect, we concluded the presence of the two closed orbits with the cross-sectional areas of 0.23% and 4.5% of the first Brillouin zone, respectively. This result was found to be inconsistent with the Fermi surface predicted from the simple band structure calculation which took into account only LUMO of M(dmit)₂.

In this study, we have observed further the magnetic-field dependence of the magnetoresistance of α-Et₂Me₂N[Ni(dmit)₂]₂ under a strong magnetic field up to 23 T in order to obtain more information about the Fermi surface of this salt. Temperature dependence of SdH effect under weaker magnetic field (B<8 T) have also been investigated in order to determine cyclotron masses of the two closed orbits which we found in the previous study.

2. Experimental

Single crystals of α-Et₂Me₂N[Ni(dmit)₂]₂ were electrochemically synthesized from an acetonitrile-acetone (1:1) solution containing Et₂Me₂N[Ni(dmit)₂] and excess Et₂Me₂NClO₄. Four-probe electrical contacts were put on samples by carbon paste. The contact resistance at the electrodes was less than 70 Ω for all samples. Resistance was measured along the a* axis which is perpendicular to the conducting sheet composed of Ni(dmit)₂. Magnetic field was applied along the a* axis.

Magnetoresistance was measured by use of two different systems. Magnetoresistance in weak field region (0 < B < 8 T) was measured by use of a lock-in amplifier with an alternating current of 10 μA in 70 Hz. Magnetic field was generated by superconducting magnet manufactured by Cryogenic Consultants Ltd. The sample temperature was controlled by pumping liquid ⁴He outside of the sample chamber in the cryostat (1.3 K < T < 4.2 K) or by electrical feed back mechanism composed of carbon resistance attached to the sample chamber and manganin heater wound on the sample chamber (4.2 K < T).

Magnetoresistance up to 23 T down to 0.5 K was measured by use of Keithly 182 Sensitive Digital Voltmeter with a DC current of 20 - 30 μA. The strong magnetic field was generated by hybrid magnet at High Field Laboratory, Institute for Materials Research, Tohoku University. The sample temperature...
a short period and the other with a long period, are visible in Fig. 2. By analyzing these data by means of Landau plot, fundamental field associated with each oscillation was estimated to be 10.6 T for the long period oscillation and 211.6 T for the short period oscillation. The above data indicate the presence of two closed orbits on the Fermi surface perpendicular to the a* axis. From the values of the fundamental fields, the extremal cross-sectional area of the closed orbit (a* orbit) associated with the long period oscillation is estimated to be $10^4 \times 10^4 \text{cm}^2$ (0.23% of first Brillouin zone) and, that of another closed orbit (b* orbit) $2.02 \times 10^4 \text{cm}^2$ (4.60% of first Brillouin zone). These results are in good agreement with those obtained in our previous study.\(^9\)

4. Magnetoresistance in High Field

Figure 3(a) shows the typical magnetoresistance data obtained at 0.5 K under the magnetic field up to 23 T. We performed the same measurements on two different sample crystals and found that the results were essentially the same for the two crystals. In each case, no hysteretic behavior was observed

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Fig. 1 Magnetic-field dependence of the resistance up to 8 T at several temperature between 1.3 K and 10.8 K. Note the scale offset between the different temperature run.

Fig. 2 Oscillation part of the resistance versus inverse magnetic field. The background resistance was subtracted by fourth-degree polynomial.

Fig. 3 (a) Magnetic-field dependence of the resistance at 1.3 K and 0.5 K up to 23 T. (b) Enlarged figure of (a) between 18 T and 23 T. Note the scale offset for both figures between the different temperature run.
against magnetic field. In Fig. 3, we note that the oscillation due to the \( \beta \)-orbit does not disappear even at a strong magnetic field as high as 2.3 T. It should be noted also that another oscillation with much shorter period appears above 11 T at 0.5 K and above 15 T at 1.3 K, indicating the presence of another larger closed orbit on the Fermi surface perpendicular to the \( a^* \)-axis. We will denote this closed orbit as the \( \gamma \)-orbit. In order to show this oscillation much clearly, the data in the magnetic field region above 18 T are drawn with an expanded scale in Fig. 3(b). As compared with the \( \beta \)-orbit oscillation, the amplitude of the \( \gamma \)-orbit oscillation markedly decreases on elevating the sample temperature from 0.5 K to 1.3 K.

We performed Fourier transformation of the oscillating data after subtracting a smooth background. This Fourier transform is expected to show a peak at the frequency corresponding to the fundamental field of each oscillation. The results are shown in Fig. 4. Both the Fourier transform of the 0.5 K data and that of the 1.3 K data show peaks corresponding to the \( \beta \) and \( \gamma \)-orbits at 216.5 and 4021 T, respectively, almost the same values of fundamental field being obtained from the Landau plot of the same experimental data. From these values of fundamental field, the extremal cross-sectional areas of the \( \beta \)- and \( \gamma \)-orbits are estimated to be 2.07 \times 10^{14} \text{ cm}^2 (4.71\% of first Brillouin zone) and 3.84 \times 10^{15} \text{ cm}^2 (87.4\% of first Brillouin zone), respectively. In Fig. 4, we can see additional two small peaks at 426 and 520 T, respectively, are accompanying a strong peak due to the \( \beta \)-orbit. The former is attributable to the second harmonics of the \( \beta \)-orbit oscillation, but the origin of the latter is unclear at present.

The value of fundamental field of the \( \beta \)-orbit derived from the high-field data is a little larger than the value, 211.6 T, obtained by the weak-field experiments. This discrepancy could come from the situation that an exact orientation of the sample crystal was rather hard to be attained in the high-field experiments because of the geometrical condition of the experimental set-up. In our previous paper, we showed that the fundamental field for the \( \beta \)-orbit was roughly proportional to \( \frac{1}{\sin \theta} \), where \( \theta \) being the angle between the bc-plane and the magnetic field direction, as expected in the case where the concerned closed orbit is on a cylindrical Fermi surface elongated along the \( a^* \)-axis. If we assume the same angular dependence for the fundamental field of the \( \gamma \)-orbit and make correction for the error in sample orientation so that the value of the fundamental field for the \( \beta \)-orbit obtained by the high-field experiments agrees with the value obtained by the weak-field experiments, thus corrected value of the fundamental field for the \( \gamma \)-orbit would be 3930 T, corresponding to the extremal cross-sectional area of 3.75 \times 10^{15} \text{ cm}^2 (65\% of first Brillouin zone).

5. Estimation of Cyclotron Mass

The amplitude of the magnetoresistance of SdH effect is expressed by Lifshitz-Kosevich formula:

\[
A = A_0 \frac{T \exp(-\lambda \mu T \lambda T / B)}{B \sinh(\lambda \mu T / B)}
\]

where \( m_m/M_e \), \( \lambda = 2 \pi^2 m_m c / e h = 14.7 \text{T}/K \), and \( T_D \) and \( m_e \) are Dingle temperature and cyclotron mass, respectively. Eq. (1) is transformed into the following two equations

\[
\ln \left( \frac{A}{T} \right) \left( 1 - \exp(-2\lambda \mu T / B) \right) = -\frac{\lambda \mu T (T + T_D)}{B} + C(B)
\]

and

\[
\ln \left( \frac{A B \sinh(\lambda \mu T / B)}{B} \right) = -\frac{\lambda \mu T_B}{B} + D(T)
\]

where \( C(B) \) and \( D(T) \) are functions of magnetic field and temperature, respectively. We have obtained \( m_e \) from the temperature dependence of the oscillation amplitude by use of Eq. (2), and \( T_D \) from the magnetic-field strength dependence of the oscillation amplitude by use of Eq. (3). The resulting values of \( m_e \) and \( T_D \) for the three closed orbits are shown in Table 1, together with the values of extremal cross-sectional area.

Table 1 The fundamental field \( B_F \), cross-sectional area \( S \), cyclotron mass \( m_c \), and Dingle temperature \( T_D \) of \( \alpha \)-, \( \beta \)-, \( \gamma \)-orbit. The value of \( T_D \) of \( \beta \)-orbit in \#5 was obtained under assumption \( m_c \cdot m_e = 0.166 \), since the temperature dependence of the oscillation amplitude is too small in the temperature range between 0.5 K and 1.3 K to determine \( m_c \) of the \( \beta \)-orbit directly from the high-field data.

<table>
<thead>
<tr>
<th>( B_F ) (Tesla)</th>
<th>( S ) ((10^3 \text{ cm}^2))</th>
<th>( S/S_{Ig} ) %</th>
<th>( m_c/m_e )</th>
<th>( T_D ) (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \alpha ) #3</td>
<td>10.6</td>
<td>1.0</td>
<td>0.23</td>
<td>0.06 \pm 0.01</td>
</tr>
<tr>
<td>( \beta ) #3</td>
<td>21.6</td>
<td>20.2</td>
<td>4.60</td>
<td>0.166 \pm 0.01</td>
</tr>
<tr>
<td>( \beta ) #5</td>
<td>216.5</td>
<td>20.7</td>
<td>4.71</td>
<td>(0.166)</td>
</tr>
<tr>
<td>( \gamma ) #5</td>
<td>4021</td>
<td>384</td>
<td>87.4</td>
<td>4.3 \pm 0.2</td>
</tr>
</tbody>
</table>

\( S_{Ig} = 4\pi^2 \hbar c = 4.39 \times 10^{13} \text{ cm}^2 \)

6. Discussions

By combining the weak-field and high-field magnetoresistance data obtained in the present study, we can conclude that the Fermi surface of \( \alpha \)-Et$_2$Me$_2$N[Ni(dmit)$_2$]$_2$ has three closed orbits, the \( \alpha \)-, \( \beta \)-, and \( \gamma \)-orbit, having the cross-sectional areas of 0.23, 4.60 and 87.4\% of the first Brillouin zone, respectively. On the other, the band structure calculation on \( \alpha \)-Et$_2$Me$_2$N[Ni(dmit)$_2$]$_2$ which took into account only LUMO of Ni(dmit)$_2$ predicted that the Fermi surface within the bc-plane was composed of a pocket-like closed orbit with the area of about 24\% of the first Brillouin zone and a pair of open orbits.
extending along the $a^\ast$-axis. Once magnetic breakdown occurs, these three orbits are expected to form a large closed orbit with an area of 100% of the first Brillouin zone. These predictions are clearly inconsistent with the results of the present magnetoresistance experiments.

Part of the authors' previously reported the results of the reflectance spectra study on $\alpha$-Et$_2$Me$_2$Ni[Ni(dmit)$_2$]$_2$, in which the optical mass in the direction of the $b$-axis was evaluated to be $5.3m_0$ ($=m_1$) and that in the direction of the $c$-axis to be $3.0m_0$ ($=m_2$) from the Drude analysis of the intra-band transition. If we adopt effective mass model apart from the band structure calculation, the cyclotron mass can be evaluated to be $(m_1/m_2)^{1/2}=4.2m_e$. This is consistent with the value of experimentally obtained cyclotron mass of $\gamma$-orbit. In fact there is the $\alpha$- and $\beta$-orbit in addition to the $\gamma$-orbit. However, since the $\gamma$-orbit occupy almost 90% of the Brillouin zone, the effect of error arising from the existence of $\alpha$- and $\beta$-orbit is negligible.

In conclusion, we have found that the two-dimensional Fermi surface of $\alpha$-Et$_2$Me$_2$Ni[Ni(dmit)$_2$]$_2$ has a large closed orbit, the $\gamma$-orbit, beside two smaller closed orbits, the $\alpha$- and $\beta$-orbit, and this fact can not be understood within the framework of the simple band structure derived only from LUMO of Ni(dmit)$_2$. Possibly, we need to take into account not only LUMO but also HOMO to get a satisfactory understanding of the band structure of this material.

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REFERENCES

9. In this paper we define Brillouin zone based on the rectangular lattice, $b=6.494$ Å; $c=13.835$ Å. The actual lattice has monoclinic symmetry: space group $C2/c$; $a=38.95$ Å; $b=6.494$ Å; $c=13.835$ Å; $\beta=99.63^\circ$; $V=3450.4$ Å$^3$. (see Ref. 7).
11. In the weak field measurement we have used the sample holder which enabled a sample to be rotated around an axis arbitrarily chosen. Thus the error of sample orientation in the weak field measurements should be smaller than that in high field measurements.