

**SINGLE-CRYSTAL GROWTH  
AND DE HAAS-VAN ALPHEN EFFECT  
IN  $\text{Yb}_4\text{Sb}_3$ \***

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(Received July 10, 2002)

$\text{Yb}_4\text{Sb}_3$  is known to show a valence fluctuation state, which is considered to relate with the high temperature phase of  $\text{Yb}_4\text{As}_3$ . To clarify an electronic state of  $\text{Yb}_4\text{Sb}_3$ , we tried to grow its high-quality single crystal and measure the de Haas-van Alphen effect. The residual resistivity ratio of the obtained single crystal was 500 and five dHvA branches were detected. Their cyclotron effective masses were in the range from  $1.8m_0$  to  $10m_0$ .

PACS numbers: 71.18.+y, 75.30.Mb

### 1. Introduction

$\text{Yb}_4\text{As}_3$  has been intensively investigated as a typical one-dimensional antiferromagnet [1]. However, the origin of the charge ordering which aligns magnetic  $\text{Yb}^{3+}$  ions along the [111] direction has not been understood so far. Madelung energy calculations [2, 3] suggest that another arrangement has lower energy than that of the actual one. As  $\text{Sm}_4\text{Bi}_3$  [4] and  $\text{Eu}_4\text{As}_3$  [5], which show the same charge ordering as that of  $\text{Yb}_4\text{As}_3$ , have quite different magnetic properties compared to that of  $\text{Yb}_4\text{As}_3$ , the magnetic interaction may be excluded as the origin of the charge ordering formation. On the other hand, it is a characteristic common to these three compounds that the hole carriers of low density dominate the conduction properties. Therefore, to understand the origin of the charge ordering, the investigation of their electronic structures will be important.

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\* Presented at the International Conference on Strongly Correlated Electron Systems, (SCES 02), Cracow, Poland, July 10–13, 2002.

The electronic structures of the charge ordered state for  $\text{Yb}_4\text{As}_3$  and  $\text{Sm}_4\text{Bi}_3$  have been rather clarified by the Shubnikov-de Haas effect (SdH). However those of their high temperature phases, which have been considered to be a thermal valence fluctuating state, are not clear, because its temperature range is too high to detect the quantum oscillation effect such as the SdH effect.

$\text{Yb}_4\text{Sb}_3$  [6] seems to be an appropriate candidate to investigate the high temperature phase of  $\text{Yb}_4\text{As}_3$ . Because the substitution of Sb for As in  $\text{Yb}_4\text{As}_3$  decreases the charge ordering temperature, and the charge ordering transition disappears in  $\text{Yb}_4\text{Sb}_3$ .  $\text{Yb}_4\text{Sb}_3$  is believed to be a valence fluctuating compound characterized by the broad peak of the magnetic susceptibility around 240K [6] and relatively large electronic specific heat coefficient ( $\gamma$ -value) of 40 mJ/molK<sup>2</sup> [7].

In this study, we grew high quality single crystals of  $\text{Yb}_4\text{Sb}_3$ , and then we investigated the electronic structure of  $\text{Yb}_4\text{Sb}_3$  by the de Haas-van Alphen (dHvA) effect.

## 2. Sample preparation and experimental details

Single crystals of  $\text{Yb}_4\text{Sb}_3$  were grown by the Bridgman method using a tungsten crucible. Ytterbium metal of 4N-purity and antimony of 6N-purity were used as raw materials. X-ray diffraction patterns revealed that single crystals have the cubic anti- $\text{Th}_3\text{P}_4$  structure with the lattice constant of 9.321Å, which is in good agreement with the previous report [6]. To observe the quantum oscillation such as the dHvA effect, very high quality single crystal is desired. The residual resistivity ratio of the obtained sample is 500.

The dHvA effect was measured by the conventional field modulation technique. A  $^3\text{He}$ - $^4\text{He}$  dilution refrigerator with a 17T superconducting magnet were used for the measurement.

## 3. Experimental results

Figure 1(a) shows a fast Fourier transformation spectrum of the dHvA oscillations for the magnetic field along the [110] direction. Five dHvA branches, their harmonics and their summations have been observed for this direction and they are denoted by  $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\delta$  and  $\epsilon$ . Figure 1(b) shows the angular dependence of the dHvA frequencies. Another branch, which its magnitude of dHvA frequency is almost same as the  $\gamma$  branch, is denoted by  $\gamma'$ . We think the same Fermi surface contributes for  $\gamma$  and  $\gamma'$  branch in comparison with other branches and the band calculation described later.

Table I displays the cyclotron effective masses estimated from the temperature dependence of the dHvA amplitude for the magnetic field along the [110] direction.

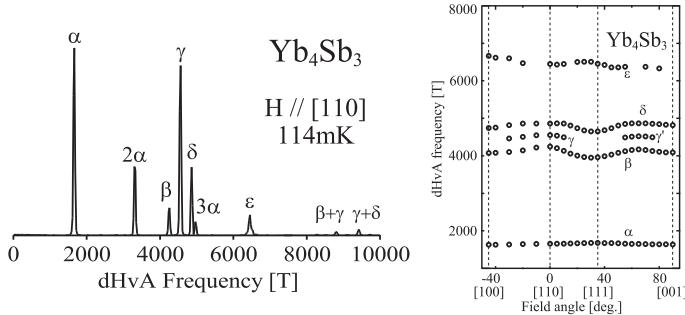


Fig. 1. (a) A fast Fourier transformation spectrum of  $\text{Yb}_4\text{Sb}_3$  for the field along the  $[110]$  direction. (b) Angular dependence of the dHvA frequencies of  $\text{Yb}_4\text{Sb}_3$ .

TABLE I  
The cyclotron effective masses of  $\text{Yb}_4\text{Sb}_3$  for the magnetic field along the  $[110]$  direction.

Branch	$F[\text{T}]$	$m_c^*[m_0]$	Branch	$F[\text{T}]$	$m_c^*[m_0]$
$\alpha$	1656	1.8	$\delta$	4860	4.9
$\beta$	4247	4.0	$\epsilon$	6448	10.5
$\gamma$	4553	4.3			

#### 4. Discussions and summary

Figure 2 shows the band structure of  $\text{Yb}_4\text{Sb}_3$  calculated by using an FLAPW method within the LDA. In the calculation, we used the lattice constant  $9.321\text{\AA}$  and  $u = 0.069$  for Yb-site ( $16c$  site in  $I\bar{4}3d$  #220) in the anti-Th<sub>3</sub>P<sub>4</sub> structure.

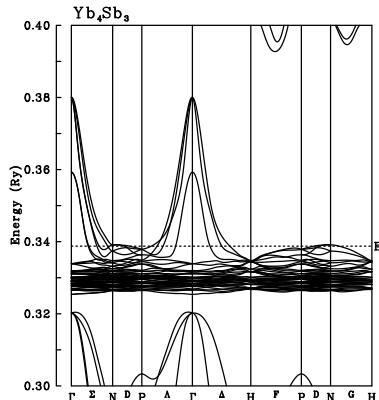


Fig. 2. Calculated electronic band structure of  $\text{Yb}_4\text{Sb}_3$ .

As shown in figure 2, the bands that consist of the 5d-character of Yb are located around the high-energy region far from the Fermi level. Near the Fermi level, the hybridized bands that consist of the 5p-character of Sb and 4f-character of Yb are located. These hybridized bands form six Fermi

surfaces with the hole character. Therefore the band calculation suggests one more Fermi surface which is not detected in our measurement. This suggestion is also supported by the experimental results. Assuming that the observed five Fermi surfaces have spherical shape, their total volume is estimated as  $1.05 \times 10^{24}/\text{cm}^3$ . Since  $\text{Yb}_4\text{Sb}_3$  has two holes per the primitive cell as suggested by the band calculation, the volume of the Fermi surface should be compared to that of the first Brillouin zone. In the meanwhile, as this crystal structure has no inversion symmetry, the spin degeneracy is solved. Therefore, the volume of the Fermi surface should be reduced to half. The reduced volume is 86% of the first Brillouin zone. On the other hand, the  $\gamma$ -value estimated from the dHvA measurement is  $31.6 \text{ mJ/molK}^2$ , which is about 80% of that estimated by the specific heat measurement. These results suggest that there are six Fermi surfaces as predicted by the band calculation. Furthermore, the obtained cyclotron effective mass is of the same order as those estimated by the band calculation. Therefore we think that the band calculation may well reproduce the outline of the electronic structure of  $\text{Yb}_4\text{Sb}_3$ . Consequently, the  $4f$  electrons of  $\text{Yb}_4\text{Sb}_3$  seem to have rather itinerant character. This is in a marked contrast to the localized character of  $4f$  electron in the high temperature phase of  $\text{Yb}_4\text{As}_3$  and its related compounds.

In summary, we grew the single crystals of  $\text{Yb}_4\text{Sb}_3$  which is considered to relate with the high temperature phase of  $\text{Yb}_4\text{As}_3$ . From the dHvA measurement and the band calculation, observed Fermi surfaces are considered to have spherical shapes and hole character. Relatively heavy cyclotron mass implies the hybridized bands that consist of the  $5p$ -character of Sb and  $4f$ -character of Yb exist.

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