6 Fermi surface of hexagonal tungsten carbide

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Abstract

The Fermi surface of hexagonal WC was proposed based on magnetoresistance and de Haas–van Alphen data taken under high magnetic fields at low temperatures. WC is a semimetal with equal numbers of electron and hole carriers of $1.5 \times 10^{21}/\text{cm}^3$. Electron Fermi surfaces are located at the point $A$ in the Brillouin zone and hole Fermi surfaces are located at the point $L$, and at the point $K$ or along the $\Gamma A$ axis.

6.1 Introduction

The transition metal carbides (TMC) are interesting because of their prominent properties such as great hardness, high electrical and thermal conductivities, stable field-electron emission\(^1\) and efficient catalysis.\(^2\) These properties are closely related to their electronic structures, yet the Fermi surfaces of TMC are not yet well established experimentally. In the case of hexagonal tungsten carbide (WC), there is only one reported experiment on the observation of de Haas–van Alphen oscillations.\(^3\)

The compound WC investigated here is simple hexagonal with a space group of $\text{P}6_3\text{m}2$ whose crystal structure and Brillouin zone are shown in Figure 6.1. The lattice parameters $a$ and $c$ are 0.2906 nm and 0.2837 nm, respectively. The carrier mobility deduced from electrical resistivity and Hall coefficient is rather high and the de Haas–van Alphen (dHvA) effect could be detected at low temperatures.\(^3\) The magnetoresistance data also give information on the compensation state and the multi-connectivity of Fermi surfaces in the Brillouin zone. In this paper, the Fermi surfaces of WC are presented and discussed on the basis of dHvA frequencies and oscillation amplitudes as well as magnetoresistance data.

6.2 Experimental

Single crystals of WC were grown by two methods; the flux method and the floating zone method. In the flux method, a mixture of 14 mol\% WC and
Co flux were melted and cooled at a rate of $4 \text{ K h}^{-1}$ from 1723 K to 1523 K and then at a rate of $100 \text{ K h}^{-1}$ from 1523 K to room temperature. The residual resistance ratio ($\rho (300 \text{ K})/\rho (4.2 \text{ K})$) (RRR) of a flux-grown WC crystal for dHvA and magnetoresistance measurements was about 70. This means that the flux-grown crystal is pure WC. Hole-doped WC crystals of large dimensions, 9 mm in diameter and 40 mm long, were obtained through the floating zone technique by adding boron in the molten zone. The composition of the molten zone and the feed rod were W:C:B = 1:0.65:0.06 and 1:1.08:0.007 (atomic ratio), respectively. The RRR value of a hole-doped WC crystal for dHvA measurements was about 20. Chemical analysis indicated that the boron content in the specimen crystal was 0.2% of the carbon content.

The magnetoresistance measurements were carried out at 1.5 K and in magnetic fields up to 10 tesla (T). The sample was a flux-grown crystal with a dimension of $2.5 \times 0.70 \times 0.45 \text{ mm}^3$, and the current direction were $\text{II}/[11\bar{2}0]$. The dc measurements were made using a standard four-probe technique.

The dHvA measurements were carried out using a field modulation technique at liquid helium temperatures and in magnetic fields up to 6 T. Second harmonic frequency signals of the pick-up coil were detected and analyzed by fast-Fourier analysis.

6.3 Results and discussion

6.3.1 Low-temperature magnetoresistance

The angular variation of the transverse magnetoresistance ($\Delta \rho/\rho_0$) of WC at 1.5 K under a constant magnetic field (H) of 5.671 T is shown in Figure 6.2, where $\Delta \rho = \rho (H) - \rho_0$, and $\rho_0$ is the residual resistivity at low temperatures. The residual resistivity of a flux-grown crystal for