de Haas-van Alphen effect in CrP

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The de Haas-van Alphen (dHvA) effect was measured for the paramagnetic compound CrP with an orthorhombic MnP-type structure using a high quality single crystal. Ten branches of dHvA frequency below 9200T are obtained in the (010) plane at 0.6K. Four frequencies in a field along the symmetry axes agree qualitatively with the theoretical results calculated with an all-electron relativistic LAPW method. The cyclotron mass ratios in two branches along the [100] axis are 4.6 and 3.1, respectively.

Key words: CrP, 3d transition metal pnictide, Pauli paramagnet, chemical vapor transport technique, dHvA effect, Fermi surface, cyclotron mass, all-electron relativistic LAPW method.

1. Introduction

3d transition metal mononpnictides with a hexagonal NiAs-like crystal structure have been investigated intensively on their various electric and magnetic properties.¹⁾ In some pnictides, there are structure phase transitions between the NiAs- and MnP-type, where the MnP-type is distorted from the NiAs-type to an orthorhombic structure, with respect to temperature, pressure and magnetic field. Since the *p*-*d* hybridization is important to understand the electronic states of these compounds, photoemission measurements were carried out with high quality samples on some of these compounds. A qualitative explanation of their magnetism was proposed in terms of their energy band calculated by an LAPW method with a local density approximation; structure phase transitions were explored in view of the nesting of their calculated Fermi surfaces.²⁾

However, since it is not easy to obtain high quality single crystals of 3d transition metal pnictides, no Fermi surface in these compounds has been yet observed experimentally. Recently, we have reported the results of de Haas-van Alphen (dHvA) effect in NiAs, as a typical Pauli paramagnet in these compounds.³⁾ The results have been interpreted in terms of hyperboloidal, distorted ellipsoidal, distorted spherical, complete spherical and octahedral surfaces, but the further analysis of the Fermi surfaces is difficult since the structure of NiAs is the orthorhombic structure below 340K. The cyclotron mass ratios are less than 1.3.⁴⁾

In Cr pnictides, CrP is a Pauli paramagnetic compound while CrAs and CrSb show a double helical magnetic order with a moment of $1.7\mu_B$ and an antiferromagnetic order with $3\mu_B$, respectively. Thus, the properties of *d* electrons could vary systematically from itinerant to localized character, as the metalloid changes from P to Sb in a 5A column of a periodic table. CrP has the MnP-type crystal structure

which is stable down to low temperature.⁵⁾

To investigate the electronic structure in CrP as the outset of the Cr pnictides, we have measured in this study the dHvA effect by a field modulation method and found ten branches of dHvA frequency. The topology of the obtained Fermi surface has been discussed and compared with a result of a band calculation.

2. Experimental and Results

The polycrystalline sample was prepared from Cr powder (99.99%) and P flakes (99.999%) by heating weighed quantities in an evacuated silica tube for 2 weeks at 800°C. The lattice constants *a*, *b* and *c* are 5.360, 3.112 and 6.016Å, respectively, determined by X-ray powder diffraction at room temperature. Because of the high melting point, it is hard to make a single crystal by means of melting, such as the Bridgman method. Hence, the single crystals were grown by a chemical vapor transport technique using I₂ as a transport agent. Approximately 1g of the CrP powder was sealed in a silica tube under vacuum, with I₂ added as 2mg/cm³. The tube was placed in a furnace in which the charge zone was maintained at 950°C and the growth zone at 800°C. After 3 weeks, the single crystals grew at the growth zone and the largest one with a size of 3 × 3 × 5mm³. The electrical resistivity ρ is 95μΩcm at 300K and shows a metallic temperature dependence. The residual resistivity ratio (RRR; $= \rho(300K)/\rho(4.2K)$) is 400.

The magnetic susceptibility χ_g was measured on the single crystal by a SQUID magnetometer. We found that the susceptibility parallel to the [100] axis is nearly equal to that perpendicular to the axis. The value of χ_g is 2.8×10^{-6} emu/g at room temperature and has a slight temperature dependence. This is in good agreement with the previous result of the powder sample.⁶⁾

The dHvA effect was measured by a field modulation method at 0.6K using a cubic sample, 1mm³, as the direction of the magnetic field was varied in the (010) plane. The field was swept from 8 to 10T at the rate of 3T/h. The ac modulation field was 2.1×10^{-3} T and the frequency was 207Hz. The observed oscillations were analyzed by a fast Fourier transform (FFT) technique. The temperature dependence of the dHvA oscillations was measured from 0.6 to 1.2K to obtain cyclotron masses.

The dHvA oscillation along the [100] direction is shown in Fig. 1 (a) and the FFT spectrum in Fig. 1 (b). The oscillation consists of two components with the frequencies 870 and 3880T. Higher order harmonic oscillation is not observed within an experimental error for both frequencies.

Fig. 1: (a) dHvA oscillation along the [100] axis at 0.6K. (b) FFT spectrum of the oscillation shown in (a). No higher order harmonic frequency is observed.

The large RRR value in this sample suggests that the Dingle temperature which represents the degree of electron scattering is small. Therefore, the cyclotron masses of the corresponding Fermi surfaces are expected to be rather heavy.

Figure 2 shows the angular dependence of the dHvA frequencies in the (010) plane, and ten branches are obtained below 9200T. As shown in Fig. 2, the α , β and γ branches are observed from 20° to 90° from the [100] direction above 3680, 3390 and 3100T, respectively. These branches are well explained by nearly ellipsoidal Fermi surfaces extending along the [001] direction.

The θ and μ branches also have their minima along the [001] direction. The μ branch is expected from a simple cylindrical Fermi surface.

There are three other branches, δ , η and λ , below 32.5° , 30° and 50° with minimum frequencies of 3880, 1657 and 870T in the [100] direction, respectively. The η branch, however, is not observed along the [100] direction as shown in Fig. 1 (b). This is probably caused by the high curvature of the corresponding Fermi surface in this direction. The θ' and κ branches are observed only in the narrow angular regions.

The cyclotron mass ratios in the δ and λ branches along the [100] axis are 4.6 and 3.1, respectively.

3. Band Calculation and Discussion

The electronic structure of MnP-type CrP was calculated by an all-electron relativistic LAPW method⁷⁾ using the lattice constants at room temperature and the position parameters reported in reference 5. In the iterative calculation, the 3d and 4s states at the Cr site and the 3s and 3p states

Fig. 2: Angular dependence of the dHvA frequencies in the (010) plane. The vertical axis is on a log scale.

at the P site are treated as valence electrons. The other electrons are calculated as core electrons. All the electrons are solved with the one-electron Dirac equation. The exchange and correlation potential is used in a local density approximation.⁸⁾ Figure 3 shows the electronic band structure of CrP in the vicinity of the Fermi level along the symmetry axes to investigate the Fermi surfaces. The Fermi level is represented by the horizontal solid line. The orthorhombic Brillouin zone for CrP is indicated in Fig. 4.

The four bands from the 21st to the 24th valence band cross the Fermi level. In the R-S line, it is found that two similar surfaces from the 21st band and the 22nd band give two maximum cross-sections around the S point and the minimum cross-sections around the R point with the field applied along the [001] direction. The dHvA frequencies for these cross sections are evaluated as the frequencies of 919, 1133, 3184 and 3837T. The latter three frequencies agree with those of the θ , γ and α branches in the [001] direction. The 24th band makes the small electron pockets near the Z point which have as frequencies 500T along the [100] direction and 600T along the [001] direction. However, these were not observed in the experiments. On the other hand, the 23rd band produces a complicated Fermi surface. In the dispersion curves of Fig. 3, there exists a Fermi surface around the Z point whose cross-section containing the Z point perpendicular to the [100] direction is estimated as 3531T. The value is close to that of the δ branch in the [100] direction.

The cyclotron mass ratios in CrP, as obtained in the δ and λ branches, are larger than that in NiAs. According to the calculated band structure of the NiAs-type 3d transition metal pnictides, there are narrow non-bonding bands

Fig. 3: Electronic band structure of CrP along the symmetry axes. The Fermi level is denoted by the horizontal solid line. The left axis indicates the energy from the bottom of the valence band on Ry and the right from the Fermi energy on eV. The bands are numbered from the bottom of the valence bands.

of 3d character between rather broad p-d bonding and anti-bonding bands.⁹⁻¹¹⁾ Calculated energy bands for the MnP-type CrP, as a whole, have the same character and the Fermi level is in the bottom part of the non-bonding bands. This is consistent with the larger cyclotron mass ratios. On the other hand, in NiAs it was found from photoemission spectroscopy that the Fermi level is in the top part of the p-d antibonding bands.¹²⁾ Thus, the small cyclotron mass ratios and the absence of the magnetic order in NiAs is probably caused by the strong p-d hybridization.

4. Conclusion

High quality single crystals of CrP ($RRR = 400$) were grown by a chemical vapor transport technique. The susceptibility of a single crystal is isotropic and weakly dependent on temperature with a broad minimum around 160K.

Ten branches of dHvA frequency are obtained in the (010) plane using this single crystal at 0.6K in the magnetic field range from 8 to 10T. The δ , η and λ branches have the minimum values of 3880, 1660 and 870T in the [100] direction, respectively. The α , β , γ and μ branches have the minima of 3680, 3390, 3100 and 520T in the [001] direction, respectively. For the α , γ , θ and δ branches among

Fig. 4: Orthorhombic Brillouin zone.

them, the frequencies along the symmetry axes are reasonably explained as the cross-section estimated by the band calculation.

The cyclotron mass ratios in the δ and λ branches are 4.6 and 3.1, respectively, and are larger than that in NiAs. These results are consistent with the calculated result for CrP that the Fermi level lies in the 3d non-bonding bands.

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