HIGH FIELD MAGNETORESISTANCE AND DE HAAS-VAN ALPHEN EFFECT

IN ANTIFERROMAGNETIC PrB_6 AND NdB_6 *

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High Field Magnetoresistance and de Haas-van Alphen Effect in Antiferromagnetic PrB_6 and NdB_6

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ABSTRACT

The transport properties and the de Haas-van Alphen (dHvA) effect have been measured for antiferromagnetic PrB_6 and NdB_6 . The number of conduction electrons is approximately one per unit cell. The magnetoresistance shows the existence of open orbits implying a multiply connected Fermi surface. The angular dependence of the magnetoresistance is roughly similar to that of the reference material, LaB_6 . The dHvA data in PrB_6 shows both paramagnetic and antiferromagnetic Fermi surfaces. The antiferromagnetic Fermi surface arises from new magnetic Brillouin zone boundaries and antiferromagnetic gaps introduced by the magnetic order, and the paramagnetic Fermi surface from magnetic breakdown through the small antiferromagnetic gaps in high field. Hybridization between the conduction electrons and the f electrons has been observed through the cyclotron masses, which in PrB_6 are three times larger than the corresponding masses of LaB_6 . In NdB_6 only the antiferromagnetic Fermi surface, quite different from those of LaB_6 and PrB_6 , has been observed.

I. INTRODUCTION

In many rare earth and actinide compounds the f electrons show a wide variety of behavior including Pauli itinerance, spin fluctuations, mixed valence and heavy fermion, and local moment magnetic order¹⁻³. The rare earth hexaborides RB_6 are an interesting series of compounds where systematic f electron behavior including many of these features can be studied. LaB_6 is a non-f electron transition metal-like system, CeB_6 is a typical Kondo substance, PrB_6 and NdB_6 are local moment metals and SmB_6 is a mixed valence compound with a gap in the narrow 4f band just at the Fermi level. Many experimental and theoretical studies are focussed on the peculiar 4f behavior of these substances.

If the 4f electrons are completely localized, R^{3+} , there is no hybridization between the 4f electrons and the conduction electrons. The Fermi surface and cyclotron mass are almost the same as those of the non-f La compounds. In this case the 4f electrons act only as scattering centers for the conduction electrons. However, as the 4f states approach the Fermi level in energy in going from Gd to Ce, the f electrons hybridize more strongly with the conduction electrons. The most highly hybridized state is expected in the Ce compound. In RB_6 the Ce compound displays a large electronic specific heat typical of f electron hybridization, yet still retains a large enough moment to order magnetically at low temperature⁴⁻⁶. The reduced moment and logarithmic like resistivity in CeB_6 are typical of the Kondo effect.

In general, the RKKY interaction competes with the Kondo effect by creating an exchange coupling between f moments which leads to magnetic order at low temperatures. As the number of f electrons increases in the RB_6 series the moment becomes larger and the RKKY interaction stronger, leading to magnetic order. temperatures which roughly follow the de Gennes relation. The antiferromagnetic ordering temperatures in CeB_6 , PrB_6 , and NdB_6 are 2.4K, 7.0K, and 7.8K, respectively⁴⁻⁷, roughly following the de Gennes relation.

The presence of the f electron in RB_6 alters the Fermi surface in three ways: through hybridization with the conduction electrons, through the f electron contribution to the crystal potential, and through the introduction of new magnetic Brillouin zone boundaries and magnetic energy gaps which occur when the f electron moments order.

The first two mechanisms alter the electronic band structure of the metal and may affect both the Fermi surface geometry and cyclotron effective masses. The two mechanisms are difficult to separate from each other, although some separation can be achieved⁸ by careful Fermi surface measurements and band structure calculations. The effect of the third mechanism can be approximated by a band folding procedure where the paramagnetic Fermi surface containing all the corrections due to hybridization and crystal potential effects is folded into the smaller Brillouin zone induced by the antiferromagnetic order. If the magnetic energy gaps associated with the antiferromagnetic structure are small enough, electrons undergoing cyclotron motion in the presence of a magnetic field can tunnel through these gaps and follow orbits on the paramagnetic Fermi surface. If this magnetic breakdown occurs, the paramagnetic Fermi surface may be observed in the de Haas van Alphen (dHvA) effect even in the presence of magnetic order. However, if there is significant hybridization or a large contribution of the f electron to the crystal potential, the paramagnetic Fermi surface geometry may be somewhat different from the non-f analog metal. Generally, one expects hybridization to appear in the dHvA results as an increased cyclotron effective mass due to the admixture of the heavier f electron with the spd conduction electrons. Such effects have been observed⁹⁻¹¹ in CeSn₃, CeCu₆, and UPt₃.

The first investigations of the Fermi surfaces of the RB₆ compounds were done on LaB₆ by Arko, et al.^{12,13} using magnetoresistance and the de Haas-van Alphen (dHvA) effect in fields up to 13.2T and temperatures down to 0.35K and by Ishizawa, et al.^{14,15} using the dHvA effect in fields up to 6T and at temperatures as low as 1.5K. The experimental results were interpreted by a Fermi surface model consisting of large electron sheets at the X point of the Brillouin zone connected by tiny necks in the X-X direction as illustrated in Figure 1. Band structure calculations carried out by Walch, et al.¹⁶ and by Hasegawa and Yanase¹⁷ confirmed the general topology of the empirical Fermi surface model but were unable to provide a quantitative explanation of all the observed orbits. However, the geometry of the electron sheets at X which contain nearly all the electrons and determine the electronic behavior were qualitatively well explained.

Systematic Fermi surface measurements on LaB₆, CeB₆, PrB₆, and

NdB₆ were first carried out by van Deursen, et al.¹⁸ for the single field direction $\langle 100 \rangle$ using pulsed fields up to 33T at temperatures down to 1.3K. They observed one frequency in CeB₆ and up to five frequencies in the other compounds which suggested the Fermi surface topology for all the compounds was similar. Later work¹⁹ on the anisotropy of the frequencies in CeB₆ and PrB₆ confirmed the existence of the X-centered ellipsoids in PrB₆ and revealed some additional features not directly analogous to LaB₆ which suggested the existence of smaller closed sheets.

An independent study of the Fermi surface of PrB₆ using the dHvA effect and magnetoresistance in fields of 15T at temperatures down to 1.4K by Onuki, et al.²⁰ provided a more complete picture of the Fermi surface geometry and effective masses in PrB₆. This work revealed two sets of low frequency orbits with the same anisotropy as those arising from the X-X neck orbits in LaB₆ but with areas approximately 100 times and 30 times larger than those in LaB₆. This more extensive data generally agreed with those of van Deursen, et al. for the areas and masses where comparison was possible.

In this paper we continue investigations of the Fermi surface properties of the RB₆ series with magnetoresistance and Hall effect measurements in CeB₆, PrB₆, and NdB₆ and with additional dHvA measurements in NdB₆ in fields up to 15T and temperatures down to 0.4K. In CeB₆ we find features characteristic of the Kondo effect. In PrB₆ we present new data on the open orbits from the magnetoresistance. In NdB₆ we present for the first time the detailed variation of the dHvA frequencies and effective masses with magnetic field direction. We compare our data for all three rare earth compounds with those of LaB₆ and discuss the implications for models of the f electron behavior.

II. EXPERIMENTAL PROCEDURES

Single crystals of RB₆ were grown by a floating zone technique. Three passes of the molten zone were made on each crystal in an atmosphere of Ar at 30 bar to prevent excessive evaporation. The typical dimensions of the resulting crystalline bars were 8 mm in diameter and 40 mm in length.

The electrical resistivity, magnetoresistance and Hall coefficient were measured by a DC method. The Hall coefficient was measured in the temperature range of 0.7K to room temperature in a field of 0.8T, where the Hall voltage was linear in the field. The magnetoresistance was measured at 1.4K in fields up to 15T. The dHvA experiments were carried out at 0.4K in fields up to 15T using field modulation and second harmonic detection. The dHvA frequencies were obtained by taking fast Fourier transforms of the oscillatory magnetization signal. Effective masses were determined from the temperature dependence of the amplitude of the signal at fixed field.

III. EXPERIMENTAL RESULTS AND ANALYSIS

The temperature dependence of the electrical resistivity of single crystal samples of RB_6 for the current along the $\langle 100 \rangle$ direction is shown in Fig. 2. The residual resistivity ratio $\rho_{RT}/\rho_{1.4K}$ is 220 in PrB_6 and 120 in NdB_6 . The inset shows the steep decrease of the resistivity below 7.0K in PrB_6 and 7.8K in NdB_6 which is due to antiferromagnetic ordering in these compounds^{6,7}. Two steps at 7.0K and 4.2K in PrB_6 correspond to the appearance of incommensurate and commensurate spin structures, respectively. The resistivity of CeB_6 shows a dense Kondo behavior, increasing logarithmically with decreasing temperature until it passes through a maximum at 4.0K and decreases quite rapidly at lower temperatures. CeB_6 undergoes two ordering transitions at 3.2K and 2.3K, where the lower one is due to the onset of antiferromagnetic order.^{4,5,21,22}

The temperature dependence of the Hall coefficient in single crystal RB_6 is shown in Fig.3. The Hall coefficient is almost temperature independent, except for the region near the ordering temperature of CeB_6 . The present results are $-(4.5 \pm 0.7) \times 10^{-4} \text{ cm}^3/\text{coul.}$ in CeB_6 , $-(3.9 \pm 1.1) \times 10^{-4} \text{ cm}^3/\text{coul.}$ in PrB_6 and $-(4.6 \pm 0.9) \times 10^{-4} \text{ cm}^3/\text{coul.}$ in NdB_6 . The Hall coefficient of LaB_6 was measured by Tanaka et al.²³ to be $-4.5 \times 10^{-4} \text{ cm}^3/\text{coul.}$ Using the lattice constants of RB_6 (R:La, 4.156 Å; Ce, 4.140 Å; Pr, 4.133 Å and Nd, 4.126 Å) we calculate the number of conduction electron per unit cell to be 1.0, 1.0 ± 0.1 , 1.2 ± 0.3 , and 1.0 ± 0.2 , respectively. These values of the electron densities are consistent with the Fermi surface of LaB_6 , which fills half the Brillouin zone with the three nearly spherical ellipsoids at

X. Band calculations of LaB_6 show that the electron states at the Fermi surface are mainly of 5d-character implying that they originate from the rare earth atom.

We show in Fig.4 the angular dependence of the transverse magnetoresistance $\Delta\rho/\rho = [\rho(H) - \rho(0)]/\rho(0)$ of RB_6 in the $\{100\}$ plane, and in Fig.5 the field dependence of the transverse magnetoresistance in selected field directions. The data of LaB_6 has been taken from ref.24. When the field is applied along the $\langle 100 \rangle$ direction, the magnetoresistance saturates at high fields in LaB_6 , PrB_6 and NdB_6 . Non-saturating behavior is observed in all other directions in the $\{100\}$ plane. For uncompensated metals like LaB_6 , this behavior is characteristic of the existence of an open orbit along the $\langle 100 \rangle$ current direction.

We have observed a complicated behavior in the magnetoresistance of PrB_6 . The magnetoresistance saturates above 100 kOe for fields directions between about 5° to 40° , and 55° to 85° from $\langle 100 \rangle$. This behavior is due to magnetic breakdown effects resulting in topological changes of the orbit and is not found in NdB_6 . The oscillatory magnetoresistance in LaB_6 is due to Shubnikov - de Haas oscillations on the small neck connecting the X-centered ellipsoids. We note that both PrB_6 and NdB_6 are in the antiferromagnetic phase for the fields and temperatures employed in the magnetoresistance experiments. Our preliminary magnetization measurements show that this antiferromagnetic phase is stable up to at least 400 kOe. We also stress that the magnitude of $\Delta\rho/\rho \sim 20$ at 150 kOe in the open orbit direction is consistent with the high field condition, $\omega_c\tau > 1$ because the relationship $\Delta\rho/\rho = (\omega_c\tau)^2$ approximately holds in the non-saturating magnetoresistance. Here, ω_c is the cyclotron frequency and τ is the relaxation time of the carrier. The value of $\omega_c\tau$ is the number of the cyclotron orbits completed between scattering events.

The magnetoresistance of CeB_6 is negative, which is characteristic to the Kondo effect. In the low field region the negative magnetoresistance is related to magnetization M by $\Delta\rho/\rho \propto -M^2$. At high fields above 100kOe, the magnetoresistance in the field direction of 23.5° increases slightly with field. We suppose that the positive magnetoresistance due to the cyclotron motion of the carriers is added to the negative magnetoresistance mentioned above. The magnetoresistance is known to become positive²⁵ at 0.5K above 50

kOe. Apparently at high enough field and low enough temperature, the magnetization dependent negative magnetoresistance saturates, leaving the positive magnetoresistance due to Fermi surface effects. In this low temperature, high field region topological information on the Fermi surface of CeB_6 could be determined.

The angular dependence and field dependence of the transverse magnetoresistance in the $\{110\}$ plane are shown in Figs 6 and 7, respectively. Non-saturating behavior due to the existence of open orbits is found in the region of $1^\circ - 10^\circ$ and $20^\circ - 35^\circ$ from $\langle 100 \rangle$ in LaB_6 . Similar behavior is observed in NdB_6 in the region of $1^\circ - 24^\circ$ and $42^\circ - 55^\circ$ from $\langle 100 \rangle$. PrB_6 does not show such non-saturating behavior in the vicinity of the $\langle 100 \rangle$ direction. The non-saturating behavior is only found in the region of 55° to 77° from $\langle 100 \rangle$. Although the $\langle 100 \rangle$ direction is the so-called singular field direction in LaB_6 and NdB_6 , it is not so in PrB_6 .

We summarize the open orbit directions derived from the magnetoresistance data in Table 1. The existence of open orbits confirms the multiply connected nature of the Fermi surface and can be understood qualitatively on the basis of the Fermi surface model of Fig. 1 as explained further below.

Finally, we show in Fig.8 the angular dependence of dHvA frequencies in RB_6 . The data of LaB_6 has been taken from refs.14 and 15. The $\langle 100 \rangle$ frequencies and the corresponding cyclotron masses which have been determined from the temperature dependence of the dHvA oscillations are tabulated in Table 2.

Although there is a great deal of detailed data concerning the Fermi surfaces of the RB_6 compounds in Fig.8, there are some systematic features which can be qualitatively understood with a simple picture. We note that there are many similarities in the dHvA data of LaB_6 and PrB_6 , but almost no similarity between the data in LaB_6 and those in NdB_6 . Close examination reveals that the α , γ , ϵ , δ , λ , and ξ branches in LaB_6 correspond in angular dependence and magnitude approximately with branches in PrB_6 . These branches have been so labeled in the data for PrB_6 in Fig.8. The other branches in PrB_6 which do not correspond to branches in LaB_6 have been labeled with arabic letters. The α frequency in PrB_6 has three branches α_1 , α_2 , and α_3 in the $\{100\}$ plane, and it degenerates into two in the $\{110\}$ plane, as is observed in LaB_6 . The cyclotron mass of the α_3 orbit in

PrB_6 , $1.95m_0$, is three times larger than the corresponding mass in LaB_6 , $0.61\text{--}0.64m_0$. Except for the ρ and ξ oscillations, all of the long range frequencies in LaB_6 are also observed in PrB_6 .

The g and g' branches in PrB_6 are very similar in shape to the ρ branches in LaB_6 but are much larger in magnitude. The dHvA frequencies of g and g' in the $\langle 100 \rangle$ direction are 5.9×10^6 Oe and 1.5×10^6 Oe, respectively, which are one hundred times and thirty times larger than 5.2×10^4 Oe as observed in LaB_6 . The masses on these orbits are $0.62 m_0$ and $0.28 m_0$, heavier than the corresponding value $0.046m_0$ in LaB_6 . In LaB_6 these branches arise from the necks which connect the X-centered ellipsoids. We propose that a similar feature exists in PrB_6 , except that there are two necks connecting each ellipsoid and the necks are appropriately larger.²⁰

The similarity of the Fermi surfaces of LaB_6 and PrB_6 is surprising because PrB_6 orders with a complicated magnetic structure involving 32 unit cells.⁶ This introduces a magnetic Brillouin zone which is much smaller than the X-centered ellipsoids. When the Fermi surface is folded into the new Brillouin zone, the large orbits such as α are interrupted by zone boundaries and should not appear in the data. We explain the similarity of the dHvA data in LaB_6 and PrB_6 by magnetic breakdown, assuming the applied field is strong enough to drive the electrons through the energy gaps created at the magnetic Brillouin zone boundaries by the antiferromagnetic structure. In that case the paramagnetic Fermi surface would be observed, and it may be similar to that of LaB_6 if the effects of hybridization and the f electron crystal potential are not too large.

The branches in PrB_6 that are not observed in LaB_6 we attribute to the antiferromagnetic Fermi surface. These branches represent the paramagnetic Fermi surface folded into the smaller magnetic Brillouin zone. With incomplete magnetic breakdown both the paramagnetic and antiferromagnetic Fermi surfaces can be seen. The a branch is the largest frequency on the antiferromagnetic Fermi surface. This signal disappears in the field range of 13° to 35° from $\langle 100 \rangle$ in the $\{100\}$ plane and 22° to 77° from $\langle 100 \rangle$ in the $\{110\}$ plane. The Fermi surface sheet giving rise to the a orbit is nearly spherical, being slightly stretched in the $\langle 110 \rangle$ direction and may possess arms which cause the orbit to disappear. These arms are probably in the $\langle 111 \rangle$ direction.

Besides the a , g and g' branches, three branches b , b' and b'' are

observed, centered at the $\langle 111 \rangle$ direction. van Deursen et al.¹⁹ observed another similar branch with a frequency of 3.7×10^7 Oe in the $\langle 111 \rangle$ direction.

The dHvA frequencies observed in NdB₆ are extremely different from those of LaB₆ and PrB₆. In fact, there are no oscillations which correspond to those of LaB₆. The characteristic features in the Fermi surface of NdB₆ are as follows. The a branch is a nearly spherical Fermi surface which is slightly stretched in the $\langle 100 \rangle$ direction. The signal of the a branch, however, disappears in the field angle of 40° to 90° from $\langle 100 \rangle$ in the $\{110\}$ plane. Moreover, it becomes extremely weak in the vicinity of the $\langle 100 \rangle$ direction, possessing a maximum amplitude at about 10° .

The g and h branches are nearly spherical ellipsoids. As there is no third branch in the $\{100\}$ plane, g and h may not be symmetry equivalent ellipsoids. The signal of the h branch seems to be degenerate with the g signal in the field range of 55° to 90° . We do not believe that the h signal simply disappears for angles greater than 55° , because its amplitude is quite strong for directions near $\langle 111 \rangle$.

The other branches are limited to small angle regions. The c branch possesses a symmetry at the $\langle 110 \rangle$ direction, the d and j branches at the $\langle 110 \rangle$ direction, and the f and k branches at the $\langle 111 \rangle$ direction.

IV. DISCUSSION

The data presented above can be understood using simple ideas for the effect of the f electron on the Fermi surface through the crystal potential, hybridization, and magnetic order. We argue that the main features of the paramagnetic Fermi surfaces of LaB₆, PrB₆, and NdB₆ are all similar, with large ellipsoids at X connected by necks in the X-X directions. Slight differences in the band structures of the three metals due to the contribution of the f electron to the crystal potential or to direct hybridization of the conduction states with the f electron alter details of the Fermi surface geometry like the shape of the ellipsoids and the size and connectivity of the necks. If significant f electron hybridization occurs, the effective masses of the paramagnetic Fermi surface are increased relative to LaB₆. When magnetic order occurs, the paramagnetic Fermi surface must be folded into the smaller

magnetic Brillouin zone, perhaps altering the observable cyclotron orbits drastically. However, if the magnetic energy gaps at the new zone boundaries are not too large, the paramagnetic Fermi surface can still be seen due to magnetic breakdown. If the applied field range spans the breakdown field, the paramagnetic and antiferromagnetic Fermi surfaces will be seen simultaneously. This case applies to PrB_6 . If the magnetic energy gaps are too large, the breakdown field will be large compared to the applied field and no magnetic breakdown will occur. In this case only the antiferromagnetic Fermi surface will be seen, as occurs in NdB_6 .

First we justify the claim that the main features of the paramagnetic Fermi surfaces of LaB_6 , PrB_6 , and NdB_6 are essentially the same. There are three reasons for this assertion. First, the value of the Hall coefficient in RB_6 is almost the same at room temperature in all three compounds. The number of conduction electrons is approximately one per unit cell, suggesting that all three metals have the ellipsoidal X-centered surfaces of LaB_6 . Even below the Néel temperature, the carrier concentration does not change in PrB_6 and NdB_6 as indicated by the temperature independent of the Hall coefficient. This temperature independence of the Hall coefficient below the Néel temperature is unusual. Secondly, the Fermi surface determined by two-dimensional angular correlation of positron annihilation radiation shows nearly the same shape for all RB_6 compounds at room temperature²⁶. The positron annihilation results show directly the existence of an electron ellipsoid at the X point. This work confirms the interpretation of the Fermi surface discussed above. Finally, we observe the α orbits arising from the X-centered ellipsoids in both LaB_6 and PrB_6 , but not in NdB_6 . However, as shown in Table 2, van Deursen et al.¹⁸ observed four dHvA signals in the $\langle 100 \rangle$ field direction in NdB_6 . Three of them corresponds to the c, g and h branches in the present experiment. The other dHvA frequency is $7.98 \times 10^7 \text{Oe}$, which corresponds to the α_3 branch of the X-centered ellipsoids. Their observation of this magnetic breakdown orbit in NdB_6 is due to their use of high fields of 29T compared to our highest field of 15T. Thus the basic feature of the LaB_6 Fermi surface is seen by dHvA measurements in both PrB_6 and NdB_6 . Based on the Hall coefficient data, the positron annihilation data, and the high field dHvA data, we conclude that the paramagnetic Fermi surfaces of all three

metals are very similar.

Despite the basic similarity in the main features of the paramagnetic Fermi surfaces of LaB_6 , PrB_6 , and NdB_6 there are small differences in the details of the geometry related to the size and connectivity of the necks. These differences can be seen in the open orbit behavior derived from the magnetoresistance data and in the dHvA data.

First we discuss the magnetoresistance. The magnetoresistance of NdB_6 in fields up to 15T is very similar to that of LaB_6 . The analogous features are as follows:

- 1) The $\langle 100 \rangle$ direction is the singular field direction.
- 2) The open orbit in the $\{100\}$ plane is found in all field directions except the $\langle 100 \rangle$ direction.
- 3) Open orbits of NdB_6 in the $\{110\}$ plane exist in the range of 1° to 24° and 42° to 55° , while the one of LaB_6 exists in the range of 1° to 10° and 20° to 35° .

In PrB_6 , open orbits are observed in the whole region of the $\{100\}$ plane except the $\langle 100 \rangle$ direction and its vicinity. Unlike in LaB_6 and NdB_6 , $\langle 100 \rangle$ is not a singular direction because there is a finite range of angles near $\langle 100 \rangle$ in which no open orbit is found. In the $\{110\}$ plane open orbits are found in only one angular range, 55° to 77° from $\langle 100 \rangle$, instead of two ranges as in LaB_6 and NdB_6 .

The angles at which the open orbits appear and disappear provide information about the placement and size of the necks in the paramagnetic Fermi surface. The open orbits on the LaB_6 Fermi surface for various field directions are shown in Fig.9. For the field near the $\langle 100 \rangle$ direction in the $\{110\}$ plane (Fig.9b) the open orbit trajectory runs between two necks in the region labelled "A". The angular region of the open orbit is restricted by the existence of these two necks. If the Fermi surface of PrB_6 is similar to that of LaB_6 , we infer that the two necks mentioned above are so large that they approximately touch each other, explaining the absence of the open orbit near the $\langle 100 \rangle$ direction in the $\{110\}$ plane in PrB_6 . The trajectory of the open orbit shown in Fig. 9 (c) is also restricted by two necks, namely one neck which the orbit must avoid near the B point and a second neck which is part of the orbit at the C point (the C neck is hidden by an ellipsoid in the view of Fig 9a). If the neck is small, this open orbit will be found at angles close to $\langle 100 \rangle$. In LaB_6 , the open orbit first appears at 20° from $\langle 100 \rangle$ in the $\{110\}$ plane. As the field

angle becomes larger than 20° , the path gradually deviates from the C neck eventually forming a closed orbit at approximately 35° . In PrB_6 , the neck is expected to be relatively large, as confirmed by the appearance of the open orbit at the rather high angle of 55° from $\langle 100 \rangle$ in the $\{110\}$ plane.

---This larger neck in PrB_6 is roughly consistent with the dHvA results. The α oscillation of PrB_6 disappears over a wider field range than in LaB_6 , as shown in Table 3, suggesting a larger neck dimension. As discussed in an earlier paper, such a result favors two interconnecting necks whose dimensions are roughly consistent with the g and g' orbits²⁰. However, the length of the necks is very short if the ellipsoid dimensions of PrB_6 are the same as those of LaB_6 . In this case we could not observe the g and g' oscillations over a wide field range or, in particular, for the field along the $\langle 100 \rangle$ direction. Therefore if the g and g' branches correspond to the necks in the paramagnetic Fermi surface, it is necessary to modify the shape of the ellipsoids in PrB_6 .

If the above analysis is also applied to NdB_6 , the neck of NdB_6 is a little larger than that of LaB_6 because the open orbit appears at 42° in the $\{110\}$ plane. This cannot be confirmed with the dHvA results, because only the antiferromagnetic Fermi surface is observed.

The magnetic breakdown phenomena that we invoke to explain the observation of the paramagnetic Fermi surface in PrB_6 can be observed on the paramagnetic Fermi surface itself. For example, for the field in the $\langle 100 \rangle$ direction the closed α_1 orbit in PrB_6 and LaB_6 should not exist because it is interrupted by a neck. However, as shown in Table 2, at sufficiently high fields the α_1 orbit can be seen, implying magnetic breakdown across the neck, a feature that has been noted in earlier dHvA and band structure studies of LaB_6 . In the antiferromagnetic state the degree of magnetic breakdown through the magnetic zone boundary gaps depends on the size of the gaps. We expect these gaps to scale roughly with the magnitude of the magnetic moment or the de Gennes factor. Apparently the magnetic fields used in our experiment are large enough to cause magnetic breakdown through the gaps in PrB_6 but are too weak to cause breakdown in NdB_6 .

Hybridization of the f electron with the conduction electrons can be seen most directly in the cyclotron effective masses. Because the f

electrons are considerably more localized than the conduction electrons, hybridization with f electrons usually lowers the Fermi velocities and raises the effective masses of the hybridized state. Thus by comparing the effective masses of analogous orbits in RB_6 , one infers the relative importance of hybridization in the metals. On the paramagnetic Fermi surface of PrB_6 the mass of the α_3 orbit is $1.95 m_0$, about three times larger than the mass of the corresponding orbit in LaB_6 . This suggests that the f electron in PrB_6 is slightly hybridized with the conduction electrons. The increased mass in PrB_6 over LaB_6 is a general feature of the paramagnetic Fermi surfaces in the two materials as shown in Fig. 10, where the mass versus frequency is plotted on a logarithmic scale. As shown, there is approximately a factor of three enhancement in all the measured masses in the two materials. If this enhancement is due to a narrowing of the bandwidth from f electron hybridization, then Fig. 10 implies that the hybridization is approximately equally strong for all the conduction electrons in PrB_6 . This general enhancement of all the masses when f electron hybridization occurs has also been seen⁹ in CeSn_3 . The paramagnetic state of NdB_6 , as measured by van Deursen et al., shows a return to the masses observed in LaB_6 , suggesting that f hybridization is absent in this metal. This interpretation is consistent with the much larger binding energy of the f electron in Nd compared to Pr.

In the antiferromagnetic state, the Fermi surface changes due to the appearance of the magnetic zone boundaries can be approximated by folding the paramagnetic Fermi surface into the smaller magnetic Brillouin zone. The magnetic structure in RB_6 may be quite complicated even though its chemical structure is simple cubic. The magnetic unit cell of PrB_6 involves 32 formula units⁶ and has a wave vector $q = (0.25, 0.25, 0.5) 2\pi/a$, while in NdB_6 there is a simple doubling⁷ of the chemical unit cell. We note that the reciprocal vector in the new magnetic unit cell of PrB_6 is not $(0.25, 0.25, 0.50) 2\pi/a$, but possesses the magnitude $1/(2\sqrt{2}) 2\pi/a$ in the $\langle 110 \rangle$ direction. Earlier attempts to account for the experimental data of PrB_6 by folding the paramagnetic Fermi surface into the magnetic Brillouin zone were not successful. A quantitative procedure using an analytical model for the Fermi surface is required to explore this procedure.

The dHvA frequency and cyclotron mass in the antiferromagnetic state of PrB_6 and NdB_6 are highly different from

those in the paramagnetic state. In PrB_6 , the a branch is the highest frequency on the antiferromagnetic Fermi surface. This signal disappears in the angular region of 12° to 35° from $\langle 100 \rangle$ in the $\{100\}$ plane and 20° to 75° from $\langle 100 \rangle$ in the $\{110\}$ plane. We suppose that the nearly spherical Fermi surface of the a branch possesses large diameter arms centered in the $\langle 111 \rangle$ direction and at 23° from $\langle 100 \rangle$ in $\{100\}$ plane. The b, b', b'' branches with a center at the $\langle 111 \rangle$ direction may be related to the arms. The carrier concentration of the nearly spherical a branch roughly corresponds to that of one ellipsoid in the paramagnetic state. As the carrier concentration does not change below the Néel temperature, the arms in the a branch and other Fermi surfaces may compensate the carrier concentration contributed by the remaining two ellipsoids.

In NdB_6 the signal of the a branch, the highest frequency in the antiferromagnetic state, disappears in the angular region of 40° to 90° in the $\{110\}$ plane, and in a narrow angular range of approximately 1° centered at $\langle 110 \rangle$ in the $\{100\}$ plane. This branch is approximately the same in area as the a branch in PrB_6 , but the angular ranges over which it disappears are different, suggesting that its topology is different from PrB_6 . Of the other branches, g and h have the strongest signals and are observed at all angles, suggesting that they arise from a nearly spherical closed sheet. The other orbits exist in finite angular ranges centered at $\langle 111 \rangle$, $\langle 110 \rangle$ or $\langle 100 \rangle$, except for the b orbit which does not appear near a symmetry direction. This pattern of orbits is not similar to that observed in PrB_6 , suggesting that the Fermi surface topology in the antiferromagnetic state of the two metals is not the same. This conclusion is consistent with the very different magnetic structure and unit cell in the two materials.

In the antiferromagnetic states of PrB_6 and NdB_6 , the masses do not follow simple scaling laws. In both materials, the masses are rather heavy, as shown by the a orbits which have masses of $2.52m_0$, and $2.00m_0$ respectively. While these masses are large compared to the non-f LaB_6 , they are not large compared to typical transition metal compounds where magnetism is observed. Therefore it is possible that the antiferromagnetic modifications to the Fermi surface band structure of these metals involve mostly d-sp hybridization.

V. CONCLUSION

We have measured the electrical resistivity, Hall coefficient, magnetoresistance and the de Haas - van Alphen effect of PrB_6 and NdB_6 to study their Fermi surface properties. The experimental results are as follows:

- 1) The Hall coefficient is temperature independent in the range of 0.7K to room temperature. The number of conduction electrons is approximately one per unit cell. This is consistent with the Fermi surface model of LaB_6 , where a set of three electron ellipsoids centered at X and connected by small necks in the X-X direction contain one electron per unit cell. Even below the Néel temperature, the carrier concentration as measured by the Hall effect does not change.
- 2) The magnetoresistance shows that both substances are uncompensated metals where the carriers are electrons. Open orbits are found at many angles in the $\{100\}$ and $\{110\}$ planes, implying a multiply connected Fermi surface in PrB_6 and NdB_6 . The $\langle 100 \rangle$ direction is a singular field direction in NdB_6 but not in PrB_6 .
- 3) In PrB_6 we have observed the antiferromagnetic Fermi surface reflecting the smaller magnetic Brillouin zone induced by the magnetic structure, as well as the paramagnetic Fermi surface which can be seen due to magnetic breakdown through the small antiferromagnetic gaps. The paramagnetic Fermi surface consists of three ellipsoids which are the same as those of LaB_6 . The necks interconnecting between ellipsoids are, however, larger than those of LaB_6 , which removes the singular field direction at $\langle 100 \rangle$. The main antiferromagnetic Fermi surface is a nearly spherical Fermi surface with arms along the $\langle 111 \rangle$ directions.
- 4) In NdB_6 , only the antiferromagnetic Fermi surface has been observed, which is highly different from those of PrB_6 and LaB_6 . The main Fermi surface is a nearly spherical sheet which is not observed over the whole angular range.
- 5) The cyclotron mass of the paramagnetic main Fermi surface (ellipsoid) in PrB_6 , $1.95m_0$, is three times larger than that of LaB_6 , $0.61\text{--}0.64m_0$.
- 6) The cyclotron masses of the antiferromagnetic main, nearly spherical Fermi surfaces in PrB_6 and NdB_6 are $2.52m_0$ and $2.00m_0$, respectively. Although these masses are slightly heavier than those in

the paramagnetic state, they are similar to those observed in other magnetic d electron metals.

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FIGURE CAPTIONS

- Fig 1: Cross section of the LaB_6 Fermi surface in the ΓXM plane. Lower case Greek letters α , γ , ϵ and ν refer to particular orbits on the surface.
- Fig 2: Temperature dependence of the electrical resistivity in RB_6 .
- Fig 3: Temperature dependence of the Hall coefficient in RB_6 .
- Fig 4: Angular dependence of the transverse magnetoresistance of (a) LaB_6 , (b) CeB_6 , (c) PrB_6 and (d) NdB_6 in the $\{100\}$ plane. The data of LaB_6 was cited from ref. 24.
- Fig 5: Field dependence of the transverse magnetoresistance of (a) LaB_6 , (b) PrB_6 and (d) NdB_6 at typical field directions in the $\{100\}$ plane. The data of LaB_6 was cited from ref. 24.
- Fig 6: Angular dependence of the transverse magnetoresistance of (a) LaB_6 , (b) PrB_6 and (c) NdB_6 in the $\{110\}$ plane. The data of LaB_6 was cited from ref. 24.
- Fig 7: Field dependence of the transverse magnetoresistance of (a) LaB_6 , (b) PrB_6 and (c) NdB_6 at typical directions in the $\{110\}$ plane. The data of LaB_6 was cited from ref. 24.
- Fig 8: Angular dependence of the dHvA frequencies in (a) LaB_6 , (b) PrB_6 and (c) NdB_6 . The data of LaB_6 was cited from refs. 14 and 15.
- Fig 9: Trajectories of the open orbits in LaB_6 . The trajectories are labelled by

the field directions shown in the figure, and the arrows show the open orbit directions.

Fig 10: Comparison of masses of LaB_6 and of the paramagnetic Fermi surface of PrB_6 .

TABLE CAPTIONS

- Table 1:** Field directions at which open orbits are observed in LaB_6 , PrB_6 and NdB_6 . The data of LaB_6 was cited from ref. 24.
- Table 2:** dHvA frequencies and cyclotron masses in (a) LaB_6 , (b) PrB_6 and (c) NdB_6 in the field along the $\langle 100 \rangle$ direction. Data by Ishizawa et al., Arko et al. and van Deursen et al. are due to refs. 14 and 15, 12 and 13, and 18 and 19, respectively.
- Table 3:** Angular ranges where the α oscillation is not observed in LaB_6 and PrB_6 . The data of LaB_6 was cited from ref. 14.

Fig. 1
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Figure 2

Figure 3

Figure 4a

Figure 4b

Figure 4c

Figure 4d

Figure 5a

Figure 5b

Figure 5c

Figure 6a

Figure 6b

Figure 6c

Figure 7a

Figure 7b

Figure 7c

Figure 8a

Figure 8b

Figure 8c

(a)

(b)

(c)

(d)

Figure 9

Figure 10

	Angle from the $\langle 100 \rangle$ direction in the $\{100\}$ plane	Angle from the $\langle 100 \rangle$ direction in the $\{110\}$ plane
LaB ₆	Whole region except the $\langle 100 \rangle$ direction	1° – 10° 20° – 35°
PrB ₆	Whole region except the $\langle 100 \rangle$ direction	55° – 77°
NdB ₆	Whole region except the $\langle 100 \rangle$ direction	1° – 24° 42° – 55°

Table 1

Onuki et al.

LaB ₆						
	Ishizawa et al.		Arko et al.		van Deursen et al.	
	Fi (x10 ⁷ Oe)	m*/m ₀	Fi (x10 ⁷ Oe)	m*/m ₀	Fi (x10 ⁷ Oe)	m*/m ₀
α ₁ & α ₂			10.09		10.03	0.7±0.1
α ₃	7.89	0.64	7.89	0.61	7.89	0.6±0.1
γ	3.22		3.22		3.24	
ε	0.85		0.86		0.83	
ρ	0.0052	0.046				

Table 2(a) Onuki et al.

PrB ₆				
	Present Results		van Deursen et al.	
	Fi (x10 ⁷ Oe)	m*/m ₀	Fi (x10 ⁷ Oe)	m*/m ₀
α ₁ & α ₂			10.14	2.1 ± 0.2
α ₃	8.19	1.95	8.09	1.6 ± 0.2
γ	3.27	1.94	3.23	1.6 ± 0.2
ε	0.94	0.94	0.94	1.1 ± 0.2
a	7.25	2.52	7.2	
f	0.79	0.66	0.82	
g	0.59	0.62	0.58	
g'	0.15	0.28		

Table 2 (b) Inuki et al.

NdB ₆				
	Present Results		van Deursen et al.	
	F _i (x10 ⁷ Oe)	m*/m ₀	F _i (x10 ⁷ Oe)	m*/m ₀
α ₃			7.98	0.6 ± 0.2
a	9.90	2.00		
c	3.44	2.43	3.39	
g	1.27	1.47	1.21	
h	0.95	1.08	0.92	1.0 ± 0.2

Table 2(€)

Onuki et al.

	LaB ₆	PrB ₆
{100}		
α_1	0° - 9°	0° - 15°
α_2	0° - 6° & 23° - 30°	0° - 12° & 26° - 40°
α_3		15° - 30°
{110}		
α_1	} 0° - 9° & 30° - 39°	0° - 5° & 30° - 40°
α_2		
α_3	68° - 75°	20° - 30° & 60° - 80°

Table 3 Onuki et al.