Electrical transport properties of stoichiometric YbP single crystal

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(Received 6 October 1997)

A large single crystal of stoichiometric YbP was grown by the mineralization method. We report the electrical resistivity, magnetoresistance, and Hall-effect measurements of this sample. These data are used to calculate the temperature dependences of the mobilities of electrons and holes as well as the carrier concentrations based on the simple two-band model. The results clearly indicate that transport properties in YbP are mainly determined by the conduction-band electrons, though an equal number of valence-band holes is present. The resistivity does not show the $-\ln T$ behavior characteristic of Kondo compounds.
[S0163-1829(98)00819-4]

I. INTRODUCTION

The ytterbium and cerium monopnictides RX_p (X_p=N, P, As, and Sb for R=Yb and X_p=N, P, As, Sb, and Bi for R=Ce) are strongly correlated electron systems with low carrier concentrations. Because of the electron-hole symmetry of the $4f$ state as well as their various puzzling properties, these two series have attracted a lot of attention in the last decade. In recent years, along with the success of preparing high-quality CeX_p single crystals, Ce monopnictides have been extensively studied with stoichiometric samples.[1] In spite of this, we are lacking in a thorough understanding of the physical properties of Yb monopnictides, in particular, the transport properties, because so far a high-quality single crystal of only YbAs was successfully prepared among the YbX_p series. Similar to Ce and other rare-earth monopnictides, all YbX_p are semimetals with a NaCl-type crystal structure. The Yb ion in these compounds is predominantly trivalent with one $4f$ hole, in which the spin-orbit split $J=\frac{7}{2}$ is the ground-state configuration and it further splits into Γ_6, Γ_8, and Γ_7 states in the cubic crystal field with Γ_6 as the ground state.[2–4] The band calculation[5] indicates that the top of the valence band formed mainly by the $p(X_p)$ state is at the Γ point of the Brillouin zone and splits into a Γ_8 quartet for $J=\frac{3}{2}$ and a Γ_6 doublet for $J=\frac{1}{2}$ through the spin-orbit interaction. The bottom of the conduction band, formed mainly by $5d$ (Yb), is at each X point, slightly overlapping with the top of the valence band to make semimetals with a low carrier concentration of the order of 0.01 per Yb ion.[6]

Since the discovery of a cooperative phase transition at around 0.5 K in YbN, YbP, and YbAs by specific-heat measurements,[7] many works have been devoted to gaining a better understanding of the low-temperature properties of these compounds. Magnetic ordering and crystalline electric-field (CEF) splitting of stoichiometric samples of YbX_p (X_p=N, As, Sb) and nonstoichiometric $YbP_{0.84}$ were investigated by means of neutron-scattering techniques.[3,8] Whereas the stoichiometric compounds YbN and YbAs showed antiferromagnetic fcc type-III order, nonstoichiometric $YbP_{0.84}$ undergoes a magnetic ordering corresponding to fcc type-II antiferromagnetism. This distinctly different behavior is supposed to be an effect of the nonstoichiometry of the sample. We have also made a systematic investigation on the thermal and magnetic properties of Yb monopnictides.[9–11] However, all these measurements were performed on stoichiometric YbN, YbAs, and YbSb, and nonstoichiometric YbP. It is very difficult to grow single crystals of YbX_p, due to the high melting point and high vapor pressure. So far, single crystals of YbX_p are prepared only for YbAs and YbP, but the YbP sample is a nonstoichiometric one.[12] This is the reason why intrinsic transport properties of YbX_p were measured only for YbAs. Clearly, in order to obtain the intrinsic transport and optical characteristics of YbP, a stoichiometric single crystal is necessary.

Recently, we succeeded in growing the stoichiometric YbP single crystal. Neutron-diffraction investigations of this sample proved the existence of long-range antiferromagnetic ordering of type II with the ordered magnetic moment $\mu_{Yb}=0.89(6)\mu_B$ and Néel temperature $T_N=0.66(1)$ K. The CEF-level scheme was established by neutron spectroscopy to be Γ_6-Γ_8 (19 meV)–Γ_7 (43.3 meV).[13] In this paper we present the results of electrical resistivity $\rho(T)$, magnetoresistance $\rho(H)$, and Hall-effect measurements performed on this high-quality YbP single crystal.

II. SAMPLE PREPARATION AND EXPERIMENT

The YbP single crystal was grown by the mineralization method in a tungsten crucible. The Yb metal of 99.9% purity (turned into small flakes in a glove box permeated with Ar gas) and P semimetal of 99.999% purity were used. Because P easily evaporates at high temperatures, a prereaction of the starting elements with a relative composition of Yb:P=1:1.1 was carried out in a closed quartz ampoule. For reaction, the

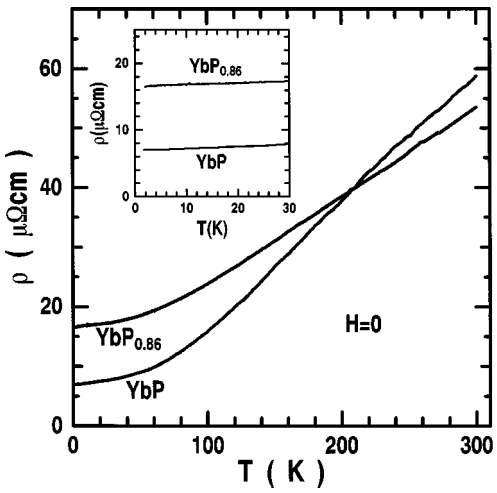

FIG. 1. Temperature (T) dependence of the electrical resistivity of stoichiometric YbP and nonstoichiometric $YbP_{0.86}$ single crystals measured at zero field. The inset shows the low-temperature linear part.

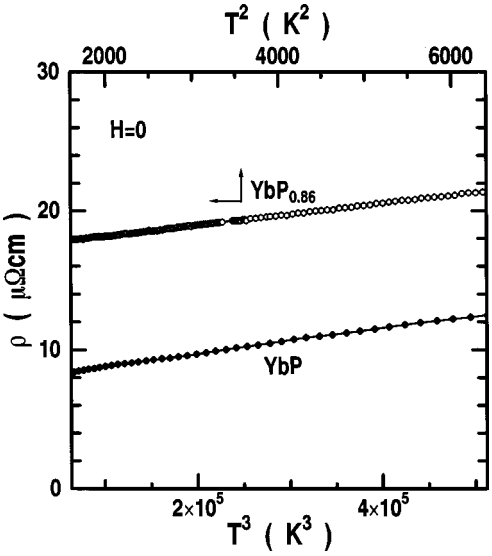

FIG. 2. $\rho(T)$ as a function of T^3 for stoichiometric YbP and $\rho(T)$ as a function of T^2 for nonstoichiometric $YbP_{0.86}$.

elements were first heated for 2 weeks up to 380 °C, and then annealed for 1 week at 700 °C to improve homogeneity. The polycrystalline material of YbP obtained by the prereaction is pressed into a hard pellet at 720 °C and 1300 atm using the glass-capsule method. This hard pellet is then sealed in a cleaned tungsten crucible using an electron-beam gun in vacuum. Finally, the crucible is slowly heated up to above 2500 °C, using a high-frequency induction furnace and kept at this temperature for 72 h. In this way, we obtained a single crystal of $5\times5\times5$ mm^3 for YbP. X-ray-diffraction patterns showed a single phase with NaCl structure. At room temperature, we determined the lattice parameter value of 5.542 Å for YbP. Chemical analysis yielded the value of 1:1.00 ±0.01 for the atomic ratio between Yb and P consistent with the neutron-diffraction results.[10] Thus we concluded that this YbP single crystal is reasonably stoichiometric.

The samples used for resistivity and Hall-effect experiments were cleaved from the large single crystal. The resistivity was measured by the standard four-probe method. Instead, for Hall-effect measurements, a four-contact geometry was used with the two voltage contacts perpendicular to the current. The samples were placed in the center of a superconducting magnet producing fields up to 10 T.

III. EXPERIMENTAL RESULTS

The temperature dependence of the electrical resistivity of the stoichiometric YbP single crystal sample is shown in Fig. 1. The data of the nonstoichiometric $YbP_{0.86}$ are also shown in this figure for comparison. For stoichiometric YbP, resistivity $\rho(T)$ increases monotonically over the investigated temperature range. Between 2 and 30 K, a linear behavior is observed (the inset of Fig. 1), while at higher temperatures, in the range about $40<T<80$ K, there is an indication of a positive curvature (concave upwards), and $\rho(T)$ approximately shows a T^3 behavior as shown in Fig. 2. With further increase of temperature, the $\rho(T)$ curve bends over a very broad temperature range centered at about 200 K, probably due to the scattering of CEF levels as observed in TmSb (Ref. 14) and stoichiometric YbAs single crystal.[12] For nonstoichiometric $YbP_{0.86}$, the temperature dependence of resistivity also shows metal-like behavior. The main differences between YbP and $YbP_{0.86}$ are the residual resistivity (RR) $[\rho_0=\rho(T\rightarrow0)]$ and residual resistance ratio (RRR) $[\rho_R=\rho(T=300)/\rho(T\rightarrow0)]$: RR is very small and RRR is much larger for the stoichiometric sample. The values of $\rho_0=6.9$ $\mu\Omega$ cm, determined by extrapolating the linear $\rho(T)$ curve at low temperatures to 0 K, and $\rho_R=8.5$ were found for stoichiometric YbP. In nonstoichiometric $YbP_{0.86}$, however, the corresponding values are $\rho_0=17.2$ $\mu\Omega$ cm and $P_R=3$. In the range of $40<T<80$ K, where $\rho(T)$ of YbP is proportional to T^3, a $\rho(T)\propto T^2$ behavior was observed for $YbP_{0.86}$ (see Fig. 2). Whereas a bend of the $\rho(T)$ curve appears around 200 K for YbP, $\rho(T)$ is almost linear in T above 150 K for $YbP_{0.86}$. Clearly, more defects present in the nonstoichiometric sample lead to larger RR and smaller RRR and smear the intrinsic features of pure YbP.

Temperature and field dependences of the magnetoresistance were measured in the transverse configuration with the current $\mathbf{I}\|[100]$ and the field $\mathbf{H}\|[010]$. The field dependence of the transverse magnetoresistance measured at 4.2 K is shown in Fig. 3 for both YbP and $YbP_{0.86}$ samples. The inset in this figure shows the plot of $[\rho(H)-\rho(0)]/\rho(0)$ vs H^2. For YbP, $\rho(H)$ increases with H in the investigated field range and roughly follows a $\rho(H)\propto H^2$ law above 2 T. A larger positive magnetoresistance (MR), $=[\rho(H)-\rho(0)]/\rho(0)$, of about 1.23 is observed at 10 T. This indicates that the stoichiometric YbP sample is a high-quality single crystal and a good compensated semimetal, which is appropriate for de Haas–van Alphen (dHvA) effect measurements. For $YbP_{0.86}$, a rather small MR value of about 0.08 at 10 T is observed due to the existence of more defects.

Figure 4 shows the temperature dependence of the resistivity measured on the stoichiometric YbP sample in the fields of 0, 3, and 7 T. Although the magnetoresistance is positive up to room temperature, the slope $\partial\rho/\partial H$ decreases as T increases. The above data can be used to calculate the carrier concentrations and the mobilities of electrons and holes as explained in next section.

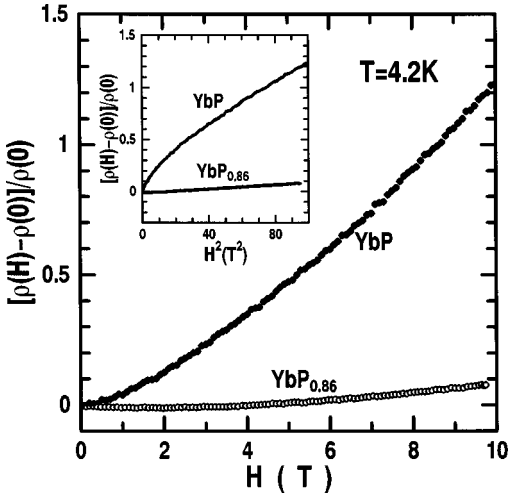

FIG. 3. Magnetic-field (H) dependence of the transverse magnetoresistance $[\rho(H)-\rho(0)]/\rho(0)$ of stoichiometric YbP and nonstoichiometric $YbP_{0.86}$ measured at $T=4.2$ K.

The temperature and field dependences of the Hall effect were also measured for the stoichiometric YbP with $\mathbf{I}\|[100]$ and $\mathbf{H}\|[010]$. As shown in Fig. 5, the Hall resistivity ρ_H is linear in H up to 7 T and almost temperature independent. Consequently, the Hall coefficient, $R_H=\rho_H/H$, is independent of H. The temperature dependence of R_H, measured in detail at $H=7$ T between 4.2 and 300 K for the stoichiometric YbP sample, is plotted in Fig. 6. The R_H is negative and constant ($=-1.37\times10^{-2}$ cm^3 C^{-1}) in the investigated temperature range. This is very different from the $R_H(T)$ behavior of stoichiometric YbAs single crystal. $R_H(T)$ in YbAs was reported to be a constant up to 20 K, then it rises rapidly above 25 K and changes sign at about 80 K, finally approaching a positive constant above 120 K.[12] We cannot explain this puzzle at this stage. The data shown in Fig. 5 together with the resistivity measurements will be used to calculate the mobilities of electrons and holes and the carrier concentrations in the following.

IV. DISCUSSION

Transverse magnetoresistivity measurements enable us to check the sample quality of a semimetal. It is well known

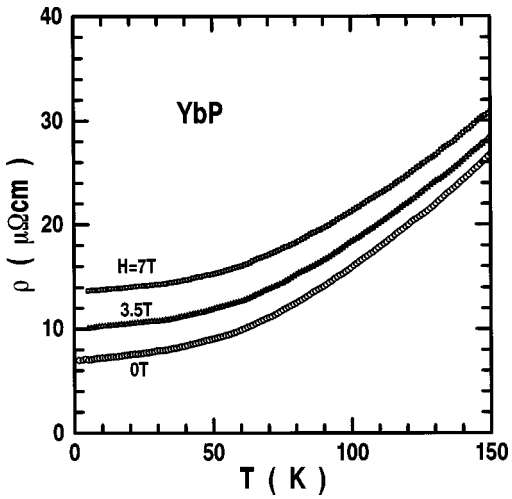

FIG. 4. Temperature (T) dependence of the resistivity of stoichiometric YbP measured at magnetic fields of 0, 3.5, and 7 T.

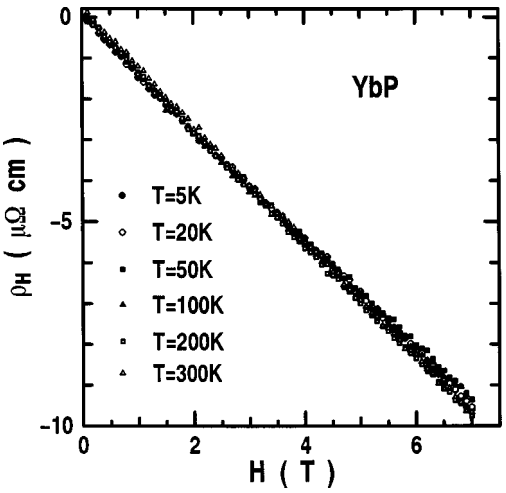

FIG. 5. Magnetic-field (H) dependence of the Hall resistivity for stoichiometric YbP measured at various temperatures T.

that lattice defects, originating from impurities or nonstoichiometry, broaden the Landau levels. When the energy interval between the Landau levels is smaller than the level broadening, then the MR is less than 1 and the dHvA or Schubnikov–de Haas (SdH) signals cannot be observed.[15] For a high-quality semimetallic single crystal, one can observe dHvA or SdH signals, large MR and RRR values, and an approximate $\rho(H)\propto H^2$ behavior. These features are observed for the stoichiometric YbP sample. In particular, MR is equal to 1.23 at 10 T is the largest value observed for any YbP single crystal so far, and the dHvA signal was first detected in our recent experiments for this YbP sample. Thus, the experimental results obtained in the present work represent intrinsic features of pure YbP.

The magnetic saturation moments in YbN, YbP, and YbAs are much smaller than the value of $1.33\mu_B$ expected from the CEF ground-state doublet Γ_6.[16] The specific-heat anomaly at the magnetic phase transition contains only about 20% of the entropy R ln2 expected from the Γ_6 doublet.[7] On the other hand, the measured exchange energy ($\sim$10 K) is an order of magnitude larger than k_BT_N.[17] Usually, these anomalies are interpreted in terms of the competition be-

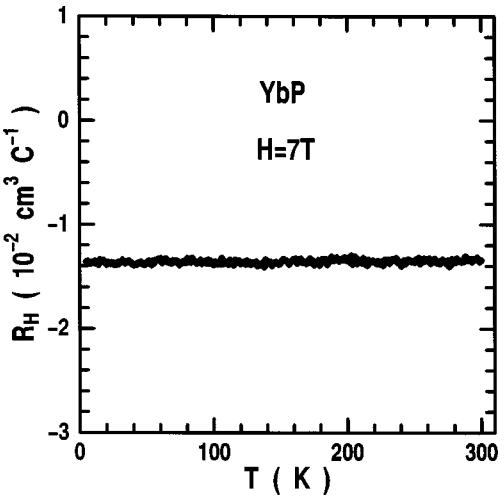

FIG. 6. Temperature (T) dependence of the Hall coefficient R_H for stoichiometric YbP measured at $H=7$ T.

tween Kondo effect and the Ruderman-Kittel-Kasuya-Yosida (RKKY) exchange interaction,[17] and Yb monopnictides are grouped with Kondo systems. However, the $-\ln T$ behavior characteristic of Kondo compounds is not detected in the resistivity of YbP (Fig. 1). According to the ''competition mechanism,'' this puzzle can be understood as follows.[12,17] The Yb monopnictides are compensated semimetals were the Kondo effect is due to the coupling between the occupied p-Γ_6 valence-hole states and the $4f$-Γ_6 hole states; this p-f mixing is the strongest at the Γ point. The resistivity, however, is mainly determined by the more mobile conduction-band electrons that have no mixing with the $4f$-Γ_6 hole states because of the symmetry.[18] Thus the nearly free conduction electrons do not participate in forming the Kondo singlet giving rise to a metal-like resistivity in YbX_p. Similar properties have been observed in YbAs.[12]

The above analysis suggests that the conduction electrons are mobile and dominate the transport properties. To separate the contributions of electrons and holes, Hall effect and magnetoresistance have been measured. Since the stoichiometric YbP sample is considered to be a well-compensated semimetal, three parameters, the concentration ($n=n_e=n_h$) and the mobilities (μ_e,μ_h) of conduction electrons and valence holes, are necessary to reproduce the electrical transport measurements. Neglecting the field dependence of the mobilities and carrier concentrations, the electrical resistivity, normal Hall constant, and transverse magnetoresistance are described in a simple two-band model as follows:[19–21]

$$1/\rho(0,T)=ne(\mu_h+\mu_e), \tag{1}$$

$$R_H(H,T)=(\mu_h-\mu_e)/ne(\mu_h+\mu_e), \tag{2}$$

$$[\rho(H,T)-\rho(0,T)]/\rho(0,T)=\mu_h\mu_eH^2. \tag{3}$$

Here, only the normal Hall effect is considered because the anomalous Hall effect is negligibly small in low-carrier rare-earth monopnictides with the exception of some mixed-valence systems.[22,23] The three parameters (n, μ_e, and μ_h), estimated from Eqs. (1)–(3), are shown in Fig. 7 as functions of temperature. The electron mobility is 3–4 times larger than the hole mobility in the investigated temperature range. This is consistent with the measured negative Hall coefficient, indicating that the resistivity of YbP is mainly determined by the electron mobility. By comparison of similar calculations for stoichiometric GdAs, GdSb, and TmSb by Li *et al.*[24,25] and for stoichiometric YbAs by Oyamada *et al.*,[12] the large mobility difference between electrons and holes $\Delta\mu=\mu_e-\mu_h$ is found only for YbP all the way up to room temperature. This is the reason why the Hall coefficient in YbP is negative and constant up to 300 K. At 4.2 K, μ_e is about 4 times larger than μ_h for both YbP and YbAs, but $\Delta\mu$ in YbAs decreases rapidly with increasing T, similar to the features observed in GdAs and TmSb. For GdSb, the electron and hole mobilities are nearly equal even at very low temperatures. These results imply that in different RX_p systems, the electron and hole mobilities are sensitively dependent on the $4f$ level, the CEF splitting, and the electronic structure. The carrier number n of YbP derived from this analysis is temperature dependent varying from $n=2.64\times10^{26}$ m^{-3} (=0.011 per Yb atom) at 4.2 K to $n=1.99\times10^{26}$ m^{-3} (=0.008 per Yb atom) at 200 K. Above about

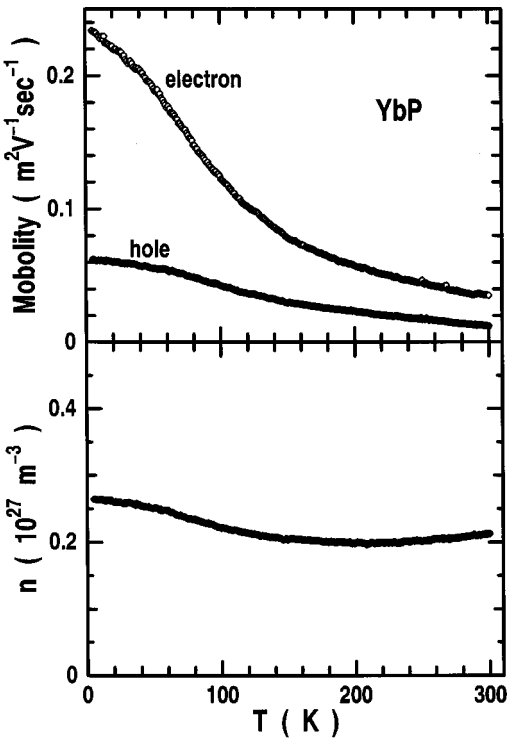

FIG. 7. Temperature (T) dependence of the mobilities (of electron and hole) and carrier concentration n calculated with the two-band model [see Eqs. (1)–(3) in the text].

200 K, n increases slowly, as observed in GdAs and GdSb. It should be noted that Eqs. (1)–(3) are applicable only for compensated semimetals. Because of the nonstoichiometry, $YbP_{0.86}$ is not a well-compensated semimetal and thus cannot be treated by an analogous calculation.

As mentioned above, the anomalous physical properties in Yb monopnictides are usually explained in terms of the competition between Kondo effect and RKKY exchange interactions. In this mechanism, the existence of p-Γ_6 holes in YbX_p is the prerequisite for the Kondo effect. However, the problem is that the p-Γ_6 hole concentration in YbX_p decreases when going from YbN to YbSb. Since the effective mass of the p-Γ_6 hole is much smaller than that of the p-Γ_8 hole, even in YbN the carrier concentration of the p-Γ_6 hole is only about 10% of the total hole-carrier number.[26] The p-Γ_6 hole contribution is negligible in the first-order approximation and so it does not lead to the Kondo effect. The p-Γ_6 hole was really not found from the dHvA measurements for YbAs.[6] In order to solve this puzzle, the magnetic polaron model developed for Ce monopnictides[27] was applied to Yb monopnictides by Kasuya.[26] In this model, Yb monopnictides are not considered as Kondo systems because the number of p-Γ_6 holes is negligibly small. Although the magnetic polaron mechanism can explain some anomalous thermal and magnetic properties of YbX_p, there is no other evidence of the formation of magnetic polarons. In particular, the resistivities of CeP and CeAs increase strongly when magnetic polarons are formed; no such behavior is found in the resistivities of YbP and YbAs. Very recently, a mechanism of paired Jahn-Teller distortion and charge-dipolar ordering was proposed and used to explain the physical properties of Yb monopnictides by Kasuya and Li.[28,29] Because this

mechanism neglects the Γ_6 Kondo effect due to the above-mentioned reason and can naturally explain most of the long-standing puzzling behavior of YbX_p, such as the unusual specific-heat peak observed near 5 K,[9] the different types of antiferromagnetic orderings at very low temperatures around 0.5 K and the substantially reduced moment,[7] etc., it currently has attracted a lot of attention.

Clearly, the strength of $p\Gamma_6$-$4f\Gamma_6$ hole hybridization is the key point with which to compare the various theoretical models. Thus, detecting the existence and the concentration of p-Γ_6 hole in YbX_p is important. In the case of YbAs the p-Γ_6 hole is not found from the dHvA measurements. Contrary to YbAs, based on the band calculation,[30] a relatively large number of p-Γ_6 holes is expected in YbP. In order to check it, dHvA measurements currently are carried out in our stoichiometric YbP single crystal; the results will be published in a forthcoming paper.

In conclusion, the transport properties of stoichiometric YbP single crystal have been investigated by measuring the resistivity, magnetoresistance, and Hall effect. These results indicate that stoichiometric YbP is a well-compensated semimetal. The temperature dependence of resistivity shows a linear behavior between 2 and 30 K, a T^3 behavior between 40 and 80 K, and a very broad bend centered at about 200 K, similar to the stoichiometric YbAs. No Kondo-type behavior is found in the resistivity. The Hall coefficient is temperature independent and is different from that observed in YbAs. A simple calculation based on the two-band model suggests that the transport properties of YbP are mainly determined by the conduction-band electrons, though an equal number of valence-band holes is present. Since the charge-dipolar ordering model, proposed very recently by Kasuya, can naturally explain some anomalous thermal and magnetic behaviors of YbX_p, it is expected that this mechanism could also give an acceptable interpretation of the above-mentioned transport properties.

ACKNOWLEDGMENTS

We wish to thank Professor T. Kasuya for helpful advice. One of the authors (D.X.L.) appreciates the financial support from the COE program of Tohoku University. This work was partially supported by the Grant-in-Aid for Scientific Research on Priority Area (No. 06244106) given by the Ministry of Education, Science, Culture and Sports, Japan.

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