Two-band conduction in superconducting $ThPt_4Ge_{12}$

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The filled-skutterudite superconductor $ThPt_4Ge_{12}$ was studied in the normal state by means of thermoelectric power, magnetoresistance, and Hall-coefficient measurements. The results indicate that this compound exhibits a two-band conductivity with strongly temperature-dependent carrier concentrations and mobilities. At low temperatures, the charge transport is dominated by the contribution due to slowly moving electrons. The experimental findings were corroborated by the results of electronic band-structure calculations performed by the relativistic full-potential local-orbital method.

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I. INTRODUCTION

Recently, we reported superconductivity in an actinoid-containing filled-skutterudite $ThPt_4Ge_{12}$ below $T_c=4.62$ K.[1] Subsequently, the superconductivity in this material was confirmed by Bauer *et al.*[2] Together with MPt_4Ge_{12},[3,4] where M=Sr, Ba, La, and Pr, $ThPt_4Ge_{12}$ forms a family of superconducting Ge-based skutterudite compounds. As regards $ThPt_4Ge_{12}$, the data obtained so far indicate that this compound can be classified as a type-II BCS-type superconductor with the Ginzburg-Landau coherence length of 35 nm, the penetration depth of 150 nm, and the upper critical field $\mu_0 H_{c2}=0.29$ T.[1] Based on the specific-heat data we determined the electron-phonon coupling constant of about 0.6,[1] being enhanced compared to those of the conventional phonon-mediated superconductors in the weak-coupling regime. Most interestingly, there are some indications of an unconventional character of the electron pairing in $ThPt_4Ge_{12}$, as in the superconducting state both the temperature dependence of the electronic specific heat C_{es} and the magnetic field variation of the Sommerfeld coefficient deviate from the predictions of the BCS theory. Furthermore, a nonstandard temperature dependence of H_{c2} was observed also for $PrPt_4Ge_{12}$.[4] Obviously, to elucidate the microscopic mechanism of superconductivity in $ThPt_4Ge_{12}$, one needs information on the electronic properties of this compound in both the superconducting region and the normal state.

Owing to high sensitivity to changes in the electronic density of states, experimental techniques probing charge transport such as thermoelectric power (TEP), magnetoresistance (MR), and Hall-coefficient (R_H) measurements are believed to be most effective in determining the type of charge carries and their concentrations and mobilities, as well as scattering mechanisms. In this work, we characterize the normal-state transport properties of $ThPt_4Ge_{12}$, by measuring TEP, MR, and R_H, and discuss the results in the framework of two-band approach. The experimentally determined band parameters such as carrier densities and mobilities and so-deduced electronic conduction mechanisms are confronted with the electronic band structure of $ThPt_4Ge_{12}$, calculated using full-potential local-orbital (FPLO) scheme.

II. EXPERIMENTAL METHODS

Polycrystalline samples used in this study were prepared and characterized as reported previously.[1] The thermoelectric power was measured in the temperature range of 5–350 K using a differential method. Temperature gradient of about 1 K was applied across the sample length and measured by a pair of fine Au(Fe 0.07%)/Chromel thermocouples. The accuracy of the measurement was estimated to be about ± 0.3 μV/K. The magnetoresistance and the Hall coefficient were simultaneously measured in the temperature range of 5–300 K by the standard ac method, on a sample with the thickness of 200 μm using a Quantum Design physical property measurement system (PPMS) platform with a horizontal rotator. Magnetic field of up to $B=\mu_0 H=9$ T was applied perpendicular to the sample surface.

The electronic band structure of $ThPt_4Ge_{12}$ was calculated by *ab initio* FPLO method within the local-density approximation (LDA).[5] The exchange-correlation potential was used in the form of Perdew and Wang.[6] The self-consistent calculations were performed for 396 k points in the irreducible Brillouin zone, assuming the experimental cubic lattice parameter $a=8.5924$ Å.[1] The thorium 7s, 7p, 6d, and 5f states and the platinum 6s, 6p, and 5d states, as well as the germanium 4s, 4p, and 3d states, were treated as valence states, whereas the thorium 6s and 6p states, the platinum 4f, 5s, and 5p states, and the germanium 3s and 3p states were included in the semicore.

III. RESULTS AND DISCUSSION

In the relativistic band structure of $ThPt_4Ge_{12}$, displayed in the upper panel of Fig. 1, one may distinguish several hybridized subsystems. The low-energy band ranging down to the binding energy of about −12 eV has a dominant 4s character due to the Ge atoms. The maximum density of these states occurs in the energy interval from −10 to −8 eV, where they hybridize with the Pt 5d states and have an admixture of the Ge 4p states. The majority of Pt 5d states are situated in the middle energy region from −6 to −2.5 eV. Here, they are accompanied by some minority contributions from the Ge 4p states. Above −3 eV the Pt 5d density gradually decreases with decreasing binding energy. As a consequence, one observes a change in the band character from d-like to p-like that appears at the energy of around −2.5 eV. Below the Fermi level the occupied states consist largely of the Ge 4p electrons. Remarkably, the contribution

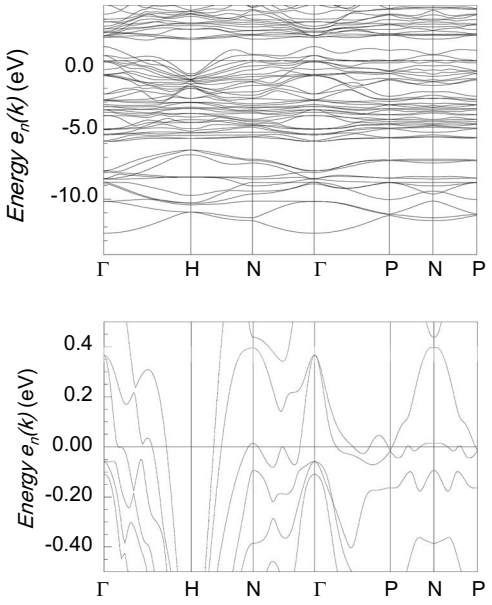

FIG. 1. Electronic bands in $ThPt_4Ge_{12}$ along selected symmetry lines within the first Brillouin zone of the body-centered-cubic lattice.

originating from the Th 6*d* and 7*s* states is visible above the binding energy of −6 eV, but it is as small as about 12% of the total density of states.

The peculiarity of the band structure of $ThPt_4Ge_{12}$ is the presence of three bands intersecting the Fermi level (see the bottom panel of Fig. 1). These bands, which are responsible for the metallic properties of the compound, mainly consist of the Ge 4*p* and Pt 5*d* states that contribute 71.8% and 13.4% of the total density of states at the Fermi level, respectively. An important feature is that the band structure of $ThPt_4Ge_{12}$ consists of antibonding bands (along the Σ and Λ lines the bands situate above the Fermi level) with four holes of the Ge 4*p* orbital and one hole derived from the Pt 5*d* orbital being predominantly located in these states. Clearly, the observed electronic band-structure features suggest $ThPt_4Ge_{12}$ to be a multiple-conduction-band compound, and it is plausible to consider, in the first approximation at least, a two-band conduction mechanism for the normal-state charge transport in this material.

The temperature dependence of the thermoelectric power of $ThPt_4Ge_{12}$ is shown in Fig. 2. The absolute TEP value of a few $\mu V/K$ is comparable with those observed for ordinary metals, such as Cu, Au, and Pb. However, the $S(T)$ curve demonstrates a rather complex behavior with a positive maximum at approximately 35 K and a negative minimum around 225 K, which cannot be adequately accounted for within a single-band conduction model appropriate for the ordinary metals. In nonmagnetic materials, TEP basically consists of contributions due to phonon drag and thermal diffusion of charge carriers. The first contribution depends on electron-phonon scattering and phonon relaxation processes, so it drops at low temperatures due to freezing out of the phonons but also decreases with increasing temperature when the normal processes of phonon-phonon scattering have an insignificant effect on the total lifetimes of thermal

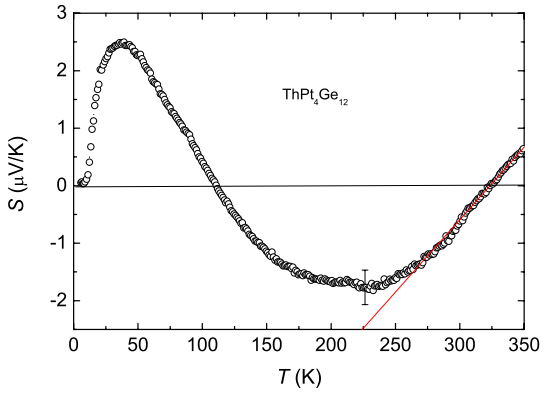

FIG. 2. (Color online) Temperature dependence of the thermoelectric power of $ThPt_4Ge_{12}$. For the sake of clarity only every 15th experimental point is displayed. The solid line emphasizes a straight-line behavior of $S(T)$ at high temperatures.

phonons. Consequently, the thermoelectric power due to phonon drag follows a T^3 dependence at low temperatures and varies as T^{-1} at high temperatures, thus leading to the formation of a characteristic maximum in $S(T)$ between $\Theta_D/10$ and $\Theta_D/3$,[7] where Θ_D is the Debye temperature. For $ThPt_4Ge_{12}$, Θ_D was found to be about 220 K.[1] Thus the observed peak at 35 K can be attributed to phonon drag mechanism.

At higher temperatures TEP should be dominated by thermal diffusion of charge carriers. As can be inferred from Fig. 2, the thermopower has negative values in the temperature range of 110–325 K and the temperature derivative dS/dT changes its sign at about 225 K. This behavior indicates that there is some contribution of the thermal diffusion of electronlike carriers, competing with that of holelike carriers. The TEP of systems with different types of charge carriers can be considered as a weighted sum of the individual contributions from each type of carriers. In the simple case of holelike and electronlike two-band system, the thermoelectric power is expressed as

$$S = \frac{\sigma_h S_h + \sigma_e S_e}{\sigma_h + \sigma_e}, \tag{1}$$

where σ_h and σ_e stand for the electrical conductivities due to holes and electrons, respectively, while S_h and S_e are the respective contributions to the measured thermopower. Clearly, in multiple-band systems $S(T)$ may have complex shapes with possible changes in the sign of TEP with varying temperature. Thus, the observed temperature dependence of the thermoelectric power of $ThPt_4Ge_{12}$ may be qualitatively understood in terms of two-band conduction.

At temperatures high enough to neglect phonon-phonon scattering, the total thermoelectric power varies in a manner derived by Mott for thermal diffusion of charge carriers,[7]

$$S_d = \frac{\pi^2 k_B^2 T}{3e} \left| \frac{\delta \ln \sigma}{\delta E} \right|_{E_F}, \tag{2}$$

where E_F stands for the Fermi energy and k_B is the Boltzmann constant. In the high-temperature limit, this formula takes a simple form:

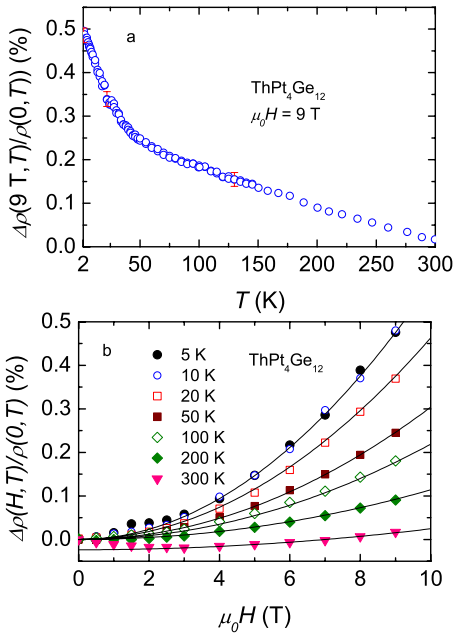

FIG. 3. (Color online) (a) Temperature dependence of the magnetoresistance of $ThPt_4Ge_{12}$ at 9 T. (b) Magnetoresistance isotherms measured at several different temperatures. The solid lines are fits of the data to Eq. (4).

$$S_d = \frac{\pi^2 k_B^2 T}{eE_F}. \tag{3}$$

Fitting of the experimental data for $T > 275$ K to a linear function $S(T) = A + BT$ yields $A = -8.15$ μV K^{-1} and $B = 0.0252$ μV K^{-2}. From this result one may derive $E_F \approx 0.295$ eV. Remarkably, the latter estimate is fairly close to the calculated energy distance of 0.35 eV from the bottom of the holelike band to the Fermi level (see the electronic structure in Fig. 1).

The transverse magnetoresistance data $\Delta\rho(B,T)/\rho(0,T) = \frac{\rho(B,T)-\rho(0,T)}{\rho(0,T)}$ of $ThPt_4Ge_{12}$ are shown in Fig. 3. Over the whole temperature range investigated MR is positive. In a field of 9 T the magnetoresistance measured at 2 K is only about 0.5% and decreases with increasing temperature in an almost linear manner up to 50 K, where it shows a distinct change in slope, and then continues a quasilinear decrease. At room temperature, in 9 T MR is less than 0.02%. The field variations of the magnetoresistance have characteristic, nearly parabolic shapes. In the case of a metal consisting of two conduction bands of holes and electrons, $\Delta\rho(B,T)/\rho(0,T)$ can be described as[8]

$$\Delta\rho(B,T)/\rho(0,T) = \mathrm{MR}_\infty(T)\frac{\mu^2 B^2}{1+\mu^2 B^2}, \tag{4}$$

where

$$\mathrm{MR}_\infty = \frac{R_h\sigma_h + R_e\sigma_e}{\sigma_h\sigma_e(R_h - R_e)^2} \tag{5}$$

and

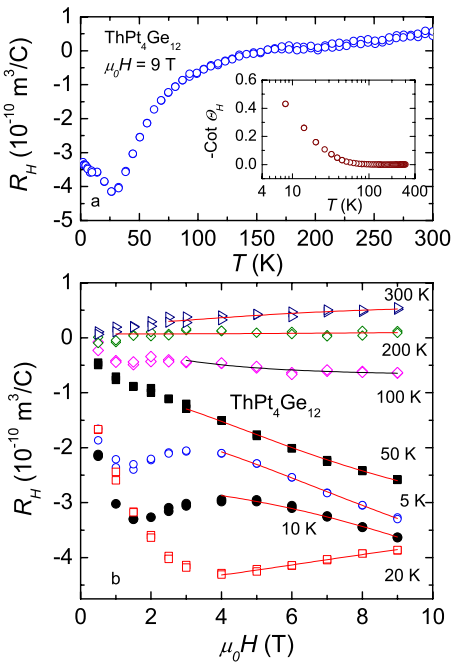

FIG. 4. (Color online) (a) Temperature dependence of the Hall coefficient of $ThPt_4Ge_{12}$ measured in a field of 9 T. The inset shows the temperature variation of the cotangent of the Hall angle. (b) Field dependencies of the Hall resistivity of $ThPt_4Ge_{12}$ taken at several selected temperatures. The solid lines are fits of the data to Eq. (7).

$$\mu = \left| \frac{\sigma_h\sigma_e(R_h - R_e)}{\sigma_h + \sigma_e} \right|. \tag{6}$$

In these expressions μ stands for the effective mobility, while R_h and R_e are the Hall coefficients due to the hole and electron contributions, respectively. As displayed in Fig. 3(b), Eq. (4) provides a proper approximation of the experimental data of $ThPt_4Ge_{12}$ (except for weak magnetic fields). The so-obtained T-dependent values of the parameters MR_∞ and μ can be used in deriving the temperature variations of the mobilities and concentrations of the electrons and holes, to be discussed below.

Shown in Fig. 4 is the temperature dependence of the Hall coefficient of $ThPt_4Ge_{12}$, measured in a field of 9 T with the electrical current of 20 mA. At room temperature $R_H(T)$ is positive and amounts to about 0.52×10^{-10} m^3 C^{-1}. With decreasing temperature R_H decreases and changes its sign around 150 K. At lower temperatures the Hall coefficient exhibits a strong temperature dependence with a negative minimum at 25 K, where it achieves a value of -4×10^{-10} m^3 C^{-1}. In this temperature region the Hall effect seems to be dominated by electrons. Within a simple one-band model, the value of R_H measured at 5 K yields the carrier density of 1.56 m^{-3}. If one takes into account the Sommerfeld coefficient $\gamma = 42$ mJ K^{-1} mol^{-1}, determined for $ThPt_4Ge_{12}$ in Ref. 1, the effective mass $m^* = \frac{3\gamma\hbar^2}{(3\pi^2 n)^{1/3}k_B^2} = 7.9m_0$ is derived, that is, a value considerably larger than that evaluated from the superconducting-state data [$5.6m_0$ (Ref. 1)]. This discrepancy is another evidence of multiband

character of the electronic transport in the compound studied.

Actually, the temperature dependence of the Hall coefficient of $ThPt_4Ge_{12}$ is totally different from those observed for ordinary metals and conventional superconductors.[9] Strongly T-dependent R_H is usually observed in magnetic systems, where charge carriers are scattered by spins carried on magnetic ions. The diamagnetic $ThPt_4Ge_{12}$ obviously cannot be considered as a representative of this group. Some temperature dependence of R_H is characteristic for high-T_c superconductors, and interpreted in terms of independent excitations of spinons and holons.[10,11] In such a case of two relaxation rates, the Hall angle cotangent is expected to follow a relation $\cot \Theta_H \propto T^2$. However, as shown in the inset of Fig. 4(a), the data of $ThPt_4Ge_{12}$ do not obey such a relation. Instead, one observes a strong increase in the absolute value of $\cot \Theta_H$ as temperature decreases below 50 K. One possibility of accounting for this behavior is to associate the $\cot \Theta_H(T)$ variation with changes in mobilities rather than with different scattering rates. This is because an increase in the magnitude of $\cot \Theta_H$ is expected when the mobilities of charge carriers decrease and/or the concentration of the charge carriers is increased. As will be shown below, in $ThPt_4Ge_{12}$ the mobilities of both electronlike and holelike carriers increase with decreasing temperature. Hence the behavior of $\cot \Theta_H$ should be associated with changes in the charge-carrier concentrations.

The change in sign of R_H near 150 K as well as strongly nonlinear field dependencies of the Hall resistivity, observed below 50 K [see Fig. 4(b)], can be straightforwardly understood within the two-band approach, applied above for interpreting the thermoelectric power and magnetoresistance data of $ThPt_4Ge_{12}$. In this model the Hall coefficient is given by the formula[12]

$$R_H(B,T) = \frac{RH_0(T) + RH_\infty(T)\mu^2 B^2}{1 + \mu^2 B^2}, \tag{7}$$

where

$$RH_0 = \frac{\sigma_h^2 R_h - \sigma_e^2 R_e}{(\sigma_h + \sigma_e)^2} \tag{8}$$

and

$$RH_\infty = \frac{-R_h R_e}{R_h - R_e}. \tag{9}$$

Fitting the experimental Hall data to Eq. (7) [see Fig. 4(b)], with the values of the effective mobility μ as derived from the analyzes of MR, one finds the parameters RH_0 and RH_∞. Then, by combining Eqs. (5), (6), (8), and (9), it is possible to calculate for each temperature the values of the particular Hall coefficients R_h and R_e as well as the conductivities σ_h and σ_e. Finally, assuming the relations $n_{(h,e)} = 1/e|R_{(h,e)}|$ and $\mu_{(h,e)} = |R_{(h,e)}|\sigma_{(h,e)}$, one obtains the temperature variations of the concentrations and the mobilities of the charge carriers in each band. The results are depicted in Fig. 5. It is found that the electron mobility is smaller than the hole mobility in the entire investigated temperature range. At 5 K μ_e amounts to 225 $cm^{-2}\,V^{-1}\,s^{-1}$ and it is over an order of magnitude smaller than μ_h. This finding implies a considerable contribution of electrons to the density of states at the Fermi level. With rising temperature the mobilities of both type of carriers strongly decrease but more dramatic change occurs for electrons: at 300 K, μ_e is only 0.5 $cm^{-2}\,V^{-1}\,s^{-1}$, being 3 orders of magnitude smaller than μ_h. In turn, the carrier concentrations in $ThPt_4Ge_{12}$ show counterpoised temperature variations: whereas n_e gradually increases with increasing temperature, n_h exhibits a decrease. At 5 K, n_e is 3 orders of magnitude smaller than that of holes, but near room temperature it is 6 orders of magnitude larger than n_h. The observed relations between the carrier concentrations reflect the behavior of the Hall coefficient of $ThPt_4Ge_{12}$, which is governed by electrons at low temperatures, yet the holes contribution becomes essential above 150 K, i.e., in the region where RH is positive.

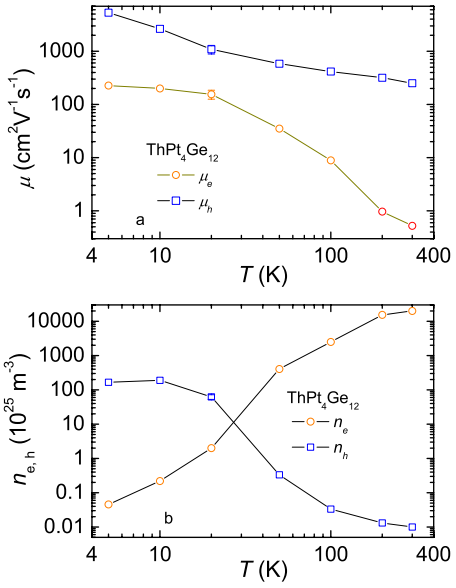

FIG. 5. (Color online) Temperature dependencies of the mobilities [panel (a)] and concentrations [panel (b)] of electrons and holes in $ThPt_4Ge_{12}$, as determined from the two-band analysis of the resistivity, magnetoresistance, and Hall-effect data.

IV. CONCLUSIONS

The thermoelectric power, transverse magnetoresistance, and Hall-effect data, measured for the filled-skutterudite superconductor $ThPt_4Ge_{12}$ in its normal state and analyzed in terms of the two-band conduction model, clearly indicate that the charge transport in this compound is governed by both electrons and holes. The electronic band-structure calculations revealed that the antibonding bands of the Ge 4p and Pt 5d are formed around the Fermi level, with predominant Ge 4p character, thus supporting the experimentally deduced scenario of mixed electron-hole-type conduction. Based on these results one may conclude that the normal-state properties of $ThPt_4Ge_{12}$ notably differ from those of conventional BCS superconductors, which usually exhibit one-band conduction.

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