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Structure and physical properties of the quaternary Remeika-phase compound $\text{Yb}_5\text{Pt}_6\text{In}_{16}\text{Bi}_2$

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We report the synthesis and characterization of an indium-rich quaternary Yb-Pt-In-Bi compound that is similar to the well-known rare-earth transition-metal stannide Remeika-phase compounds. In addition to structural/composition studies identifying the compound as $\text{Yb}_5\text{Pt}_6\text{In}_{16}\text{Bi}_2$, we have made dc and ac magnetic susceptibility, specific heat, resistivity, magnetoresistance, Hall effect, and thermoelectric power measurements on this material. It appears that this Remeika-phase compound (structure type $\text{Tb}_5\text{Rh}_6\text{Sn}_{18}$) is moderately disordered. Crystal-field effects influence the temperature dependence of the dc magnetic susceptibility, the specific heat, the resistivity, and the thermoelectric power. A cusp in the ac magnetic susceptibility peaks near 300 mK, close in temperature to where the specific heat divided by temperature $C_p(T)/T$ also reaches a maximum. The susceptibility feature is frequency dependent and suggestive of a disorder-induced spin-glass transition rather than conventional magnetic order.

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INTRODUCTION

Since being discovered in the early 1980s,^{1–3} Remeika-phase compounds (tin-rich rare-earth transition-metal stannides) have attracted much attention, especially because of the coexistence of magnetism and superconductivity that is observed in some members of this family of compounds.⁴ Although distorted versions of each exist,^{5,6} the materials can be divided into two groups. The first are those derived from a face-centered-cubic structure with lattice constant $a \approx 9.7 \text{ \AA}$, such as $R_3M_4\text{Sn}_{13}$, often written $\text{Sr}R_3M_4\text{Sn}_{12}$ because of the multiplicity of Sn sites, where R is a rare earth and M is a transition-metal element. The more complicated group are those derived from a face-centered-cubic structure with $a \approx 13.7 \text{ \AA}$, for example $R_5M_6\text{Sn}_{18}$ or $\text{Sn}_{1-x}R_xR_4M_6\text{Sn}_{18}$. Both classes of compounds form with many different rare earths and transition metals.⁴ We have found that it is also possible to synthesize indium-rich compounds in the same structure that seem to share many of the physical properties of these stannides. Here, we report the observation of the larger-cell structure in an Yb-Pt-In-Bi quaternary phase. We also have observed the smaller-cell phase in rare earth-platinum-indium ternaries.⁷ The only previously reported group of such compounds that do not contain Sn are the rare-earth transition-metal germanides, discussed by Braun.⁸

SYNTHESIS AND STRUCTURAL CHARACTERIZATION

In an attempt to grow single crystals of Yb-Bi-Pt phases from an indium flux,⁹ we have grown single crystals of a quaternary phase Yb-Pt-In-Bi compound. The crystals grow from an approximately 10 molar % solution of the composition YbBiPt in excess In. The synthesis is made in alumina crucibles encapsulated in evacuated silica, by slow cooling from 1100 °C. Multi-faceted crystals with faces up to 1 cm in

lateral dimension grow from these melts. They have an appearance and morphology very similar to what is found in the growth of the Remeika stannides from excess Sn. The crystals are clearly quaternary phases as it is not possible to synthesize the material from melts that exclude any of the constituent elements (in particular Bi). Furthermore, it has not proved possible to synthesize the Yb-Pt-In analogue of the 9.7-Å fcc stannide, although such a phase can be produced with light rare earths, for example $\text{Ce}_3\text{Pt}_4\text{In}_{13}$.⁷

The symmetry of the Yb-Pt-In-Bi crystals was established from precession photographs using $\text{Mo}_{K\alpha}$ radiation. The photographs display Laue symmetry $m3m$ and reflection conditions $hkl: h+k, h+l, k+l=2n, 0kl: k, l=2n, hhl: h+l=2n, h00: h=2n$, consistent with the space groups $F432$, $F43m$, and $Fm-3m$. The F cell parameter, determined from the precession photographs, is $a \approx 13.8 \text{ \AA}$. Crushed crystals also were examined by powder x-ray diffraction, using a Siemens diffractometer and $\text{Cu}_{K\alpha}$ radiation, in order to determine accurately the cell constant. The final lattice constant, refined by the least squares method using the absolute θ angle of 12 high angle reflections, was $a = 13.86(2) \text{ \AA}$.

Quantitative x-ray microanalysis was performed by applying the Cliff-Lorimer ratio technique¹⁰ to data obtained with a Phillips CM 300 transmission electron microscope (TEM) operating at 300 kV and equipped with a Kevex x-ray energy-dispersive (XEDS) analysis system. The Cliff-Lorimer (or sensitivity) factors, k , used in the XEDS analysis, were determined from analysis of the stoichiometric standard compounds YbBiPt and YbInCu_4 . TEM samples of Yb-Pt-In-Bi and of the standard compounds YbBiPt and YbInCu_4 were prepared by crushing single crystals of each compound in anhydrous methanol, dispersing them onto a 1000-mesh TEM grid, and immediately inserting them into the microscope, in order to avoid potential contamination. “Beam transparent” areas along the edges of many crystal-

lites of each compound were examined to check both the homogeneity and the stability of the specimen. All the crystallites were studied under kinematical diffraction conditions. The XEDS spectra for both standards and the unknown compound Yb-Pt-In-Bi were acquired, interpreted, and processed with the DTSA software package¹¹ under identical acquisition conditions of electron-beam energy, detector efficiency, position and orientation of the specimen relative to the detector, and with 1000 s collection times. Because of the strong overlap of the Bi *L* lines with the Pt *L* lines, the k_{BiYb} and k_{PtYb} factors were determined from the integrated intensities of the Pt M_4 (2202 eV), M_5 (2122 eV) and of Bi M_4 (2688 eV), M_5 (2580 eV) lines; the use of these low-energy lines introduced a $\pm 5\%$ error in their determination. The composition of the Yb-Pt-In-Bi sample was found to be 43.07 wt. % In, 19.69 wt. % Yb, 26.85 wt. % Pt, 10.08 wt. % Bi, corresponding to the chemical formula $\text{Yb}_5\text{Pt}_6\text{In}_{16}\text{Bi}_2$. No inhomogeneities were observed.

The x-ray diffraction and XEDS data suggest that the material belongs to the $\text{Tb}_5\text{Rh}_6\text{Sn}_{18}$ type structure described by the space group $Fm-3m$. Rietveld refinement of single-crystal neutron-diffraction data confirms this suggestion and indicates that the compound is disordered (i.e., variations in site occupancy are observed). Such disorder is a ubiquitous feature of the Sn variants of these compounds.⁵ For simplicity, we assume in what follows that the compound we are studying has the composition $\text{Yb}_5\text{Pt}_6\text{In}_{16}\text{Bi}_2$. It is important to note that this composition would require two distinct Yb sites even in the absence of disorder. In the $F-43m$ space group, a less favorable choice based on the larger *R* factor in our neutron-diffraction studies, this possibility is easily realized as one fully-occupied Yb site with a unit-cell multiplicity of four (that one infers from magnetic susceptibility to contain magnetic Yb^{+3} ions) and one fully-occupied site with a multiplicity of one containing nonmagnetic Yb^{+2} . In the case of $Fm-3m$, partial occupancy of an eight-fold site and partial occupancy of a one-fold site is required. Although the latter choice may be less natural in obtaining four trivalent Yb's and one divalent Yb per formula unit (as suggested by the magnetic susceptibility data discussed below), it does provide a natural source of disorder and frustration, consistent with the spin-glass behavior we observe at low temperature. More work is clearly required to differentiate rigorously between the $F-43m$ and $Fm-3m$ space groups.

A broad range of experimental techniques was used to characterize the physical properties of $\text{Yb}_5\text{Pt}_6\text{In}_{16}\text{Bi}_2$. The dc magnetic susceptibility was measured using a commercial SQUID magnetometer. The heat capacity above 2 K was measured using a thermal relaxation technique; low-temperature ac magnetic susceptibility and heat capacity were measured in a dilution refrigerator using mutual inductance and semiadiabatic heat-pulse techniques, respectively. Transport measurements were performed in a He^4 cryostat and a dilution refrigerator using the standard four-wire ac technique.

EXPERIMENTAL RESULTS AND DISCUSSION

The magnetic susceptibility of $\text{Yb}_5\text{Pt}_6\text{In}_{16}\text{Bi}_2$ measured in a field of 1000 Oe is shown in Fig. 1. Fitting the data above 100 K to a Curie-Weiss law yields an effective moment of

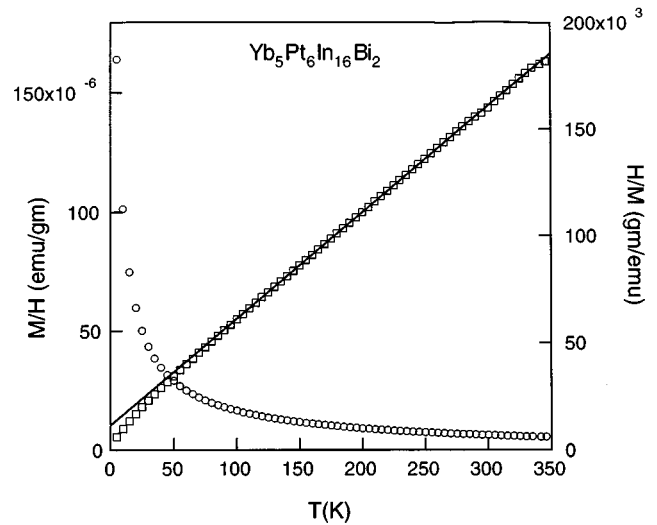


FIG. 1. The temperature-dependent magnetic susceptibility (open circles) and the inverse magnetic susceptibility (open squares). The solid line is a Curie-Weiss fit to the high-temperature data.

$3.72\mu_B/\text{Yb}$, an anomalously low value, and a Weiss temperature $\theta_{\text{CW}} = -27$ K. However, if we assume that one Yb per formula unit is nonmagnetic, i.e., divalent Yb, then the effective moment per trivalent Yb is $4.15\mu_B$, a number close to the free-ion Hund's rule value of $4.54\mu_B$. Below 100 K, the deviation from the extrapolated high-temperature Curie-Weiss behavior suggests a crystal-field splitting of the ground state multiplet of trivalent Yb atoms. We have synthesized the corresponding Gd-Pt-In-Bi compound for comparison. Assuming the $\text{Gd}_5\text{Pt}_6\text{In}_{16}\text{Bi}_2$ stoichiometry, we find from its magnetic susceptibility an effective moment of $7.96\mu_B/\text{Gd}$, essentially the free-ion value, with all 5 Gd atoms being magnetic. This adds support to our assumption regarding the presence of one divalent Yb site in $\text{Yb}_5\text{Pt}_6\text{In}_{16}\text{Bi}_2$.

The low-temperature specific heat of $\text{Yb}_5\text{Pt}_6\text{In}_{16}\text{Bi}_2$ is shown in Figs. 2 and 3. Note that to facilitate a comparison with the magnetic susceptibility data we have normalized the

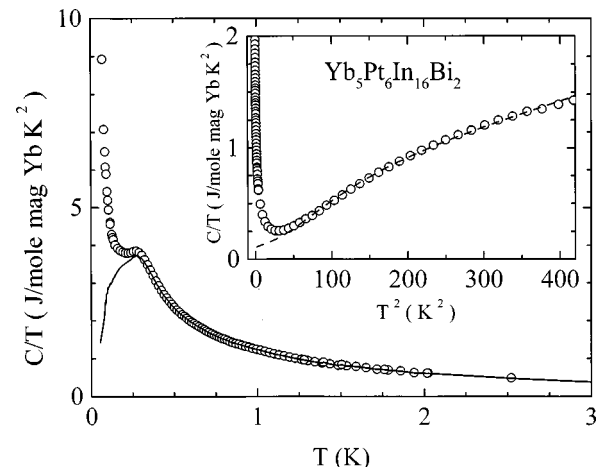


FIG. 2. C/T vs temperature (open circles) and C_{mag}/T vs temperature (solid line). C/T vs T^2 is shown in the inset for $T \leq 20$ K. The dashed line is a fit to the high-temperature data.

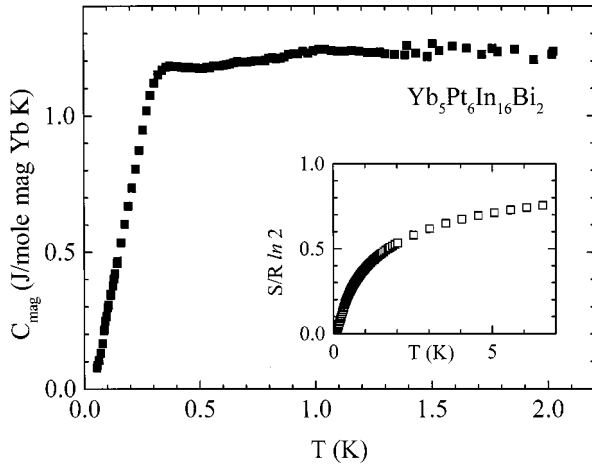


FIG. 3. C_{mag} vs temperature below 2 K. The temperature-dependent magnetic entropy is pictured in the inset.

specific heat data per mole of magnetic Yb. The inset to Fig. 2 shows the data plotted as C/T vs T^2 . The data show a modest downward curvature above 5 K, indicative of a crystal-field level influencing the specific heat. A fit to the data for $5 \text{ K} < T < 20 \text{ K}$ (dashed line) yields a Sommerfeld coefficient γ of $107 \pm 3 \text{ mJ/mole mag Yb K}^2$, a phonon contribution βT^3 with $\beta = 2.5 \text{ mJ/mole mag Yb K}^4$ ($\theta_D = 178 \text{ K}$) and a quartet crystal-field level located $58 \pm 2 \text{ K}$ above a doublet ground state. It should be pointed out that in the $\text{Tb}_5\text{Rh}_6\text{Sn}_{18}$ structure, the point symmetry of Yb in $\text{Yb}_5\text{Pt}_6\text{In}_{16}\text{Bi}_2$ causes the $J = 7/2$ Yb multiplet to split into four doublets. The fact that we obtain the best fit to our specific heat data with a doublet-quartet configuration suggests the presence of two close-in-energy excited doublets. In fact, fits which allow three crystal-field levels produce nearly degenerate excited doublets (not shown), but with large uncertainties in the fitted values due to the large number of free parameters in the fits.

C/T rises continuously below 5 K. The low-temperature data are shown in the main part of Fig. 2, where C/T is plotted as a function of T below 3 K. A maximum, too broad to be consistent with conventional magnetic order, is seen near 300 mK. The subsequent rise in specific heat at the lowest temperatures appears to be due to a nuclear Schottky contribution, because the data can be well fit by a $1/T^2$ term. The magnetic specific heat, C_{mag} , was determined by subtracting the fitted low-temperature nuclear-Schottky contribution and the fitted high-temperature electronic, phonon, and crystal-field contributions (these contributions are given by the dashed-line fit in the inset of Fig. 2) from the total specific heat. The quantity C_{mag}/T is shown by the solid line in Fig. 2 and is replotted as C_{mag} vs T in Fig. 3. The sharp rise of C_{mag} between 0.1 and 0.3 K is followed by a plateau of almost constant specific heat up to 1 K and only a slight subsequent decrease at higher temperature. Because only $0.75 R \ln 2$ of magnetic entropy is recovered by 7 K, a splitting of the doublet ground state of Yb^{3+} ions due to conventional magnetic order below 1 K may be excluded.

Indeed, subsequent χ_{ac} measurements at different frequencies confirm the existence of a spin-glass-like transition below 0.3 K. In Fig. 4(a) we show the real part $\chi'(T)$ of the complex ac magnetic susceptibility measured on a single

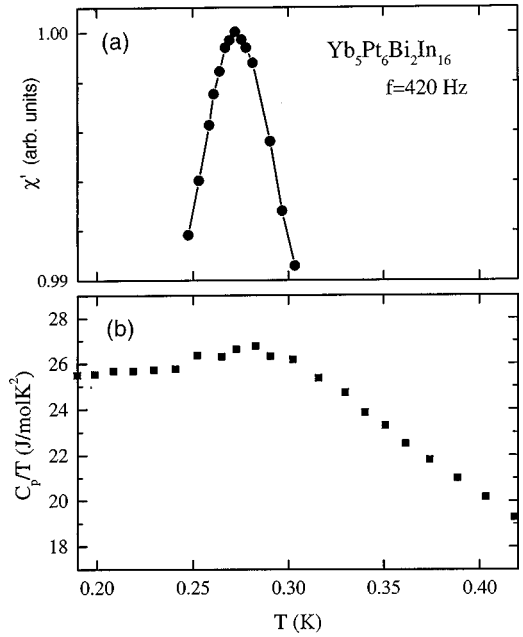


FIG. 4. Temperature dependences, between 0.2 and 0.4 K, of the real part of the complex ac magnetic susceptibility (upper panel) and specific heat divided by temperature as a function of temperature (lower panel), measured on the same single crystal.

crystal of $\text{Yb}_5\text{Pt}_6\text{In}_{16}\text{Bi}_2$ between 0.2 and 0.4 K. At a frequency of 420 Hz, a distinct but relatively broad maximum is observed at 0.27 K, suggesting a freezing of magnetic moments. An external field of 100 Oe parallel to the ac excitation field, of order 0.1 Oe, further broadens the maximum. In Fig. 4(b) we show the ratio of specific heat at constant pressure divided by temperature, $C_p(T)/T$, for the same crystal over the same temperature range. The maximum in $C_p(T)/T$, indicating the maximum rate of loss of entropy, is very close in temperature to the $\chi_{\text{ac}}(T)$ maximum.

We also have measured $\chi'(T)$ for several other excitation frequencies between 18 and 1011 Hz. The temperature T_f at which χ' reaches a maximum increases with increasing frequency ν , again typical of spin-glass behavior. In our case the variation of T_f with frequency can be described adequately using the Vogel-Fulcher relation

$$\nu(T_f) = \nu_0 \exp\{-E_a/[k_B(T_f - T_0)]\}, \quad (1)$$

where $\nu_0 = 1 \times 10^{13} \text{ s}^{-1}$ is chosen as the characteristic frequency.¹² The T_f versus $1/\ln(\nu_0/\nu)$ data plotted in Fig. 5 can be fit by a straight line with $T_0 = 0.19 \text{ K}$ and an activation energy E_a/k_B of 1.9 K. Over the range of frequencies for which we measured T_f , the average value of $T_0/T_f \approx 0.68$ indicates that $\text{Yb}_5\text{Pt}_6\text{In}_{16}\text{Bi}_2$ is a spin glass with a moderate strength of RKKY interaction between magnetic moments, mediated by conduction electrons.¹²

The absence of conventional long-range order in $\text{Yb}_5\text{Pt}_6\text{In}_{16}\text{Bi}_2$ is most likely due to the inherent disorder in the Yb sublattice. The ratio T_f/θ_{CW} , where θ_{CW} is the high-temperature Weiss temperature extracted from dc magnetic susceptibility, is of the order of 0.01, suggesting a high degree of frustration. The rather small entropy associated with the freezing transition, however, indicates that either only a small fraction of full-moment Yb ions is affected by the

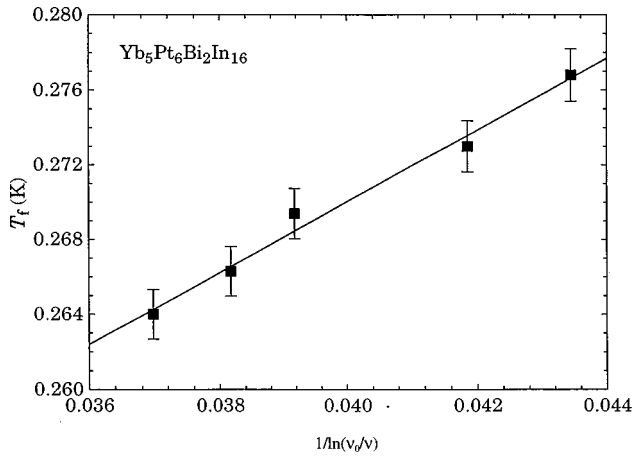


FIG. 5. Temperature at which the real part of the complex magnetic susceptibility reaches a maximum as a function of reduced frequency. The solid line is a fit to the Vogel-Fulcher relation. See text for details.

freezing or considerably reduced Yb moments are frozen out. The present set of experiments cannot distinguish clearly between these two cases.

The temperature dependence of the electrical resistivity of $\text{Yb}_5\text{Pt}_6\text{In}_{16}\text{Bi}_2$ is shown in Fig. 6. The resistivity drops by only 4% between 300 and 50 K, then rises approximately 15% at low temperature, going through a broad maximum in the region of the spin-glass transition. The origin of the rise in resistivity below 50 K is not clear; however, the field-dependent magnetoresistance (MR), defined as $\Delta\rho/\rho_0 = [\rho(H) - \rho(0)]/\rho(0)$, shown in Fig. 7(a) obeys the simple scaling relationship described by Beal-Monod and Weiner¹³ for a Kondo system with $T \gg T_K$: $\Delta\rho \propto f(M)$, where M is the magnetization. By plotting the magnetoresistance vs $M \approx H/(T + \theta)$ [Fig. 7(b)], all of the data collapse on a universal curve for $\theta \approx 1$ K. Hence, the MR is consistent with a low characteristic energy scale in this compound.

The temperature-dependent Hall coefficient, measured in 10 kOe, is shown in Fig. 8 as R_H^{-1} versus T . R_H is negative at all temperatures and is strongly temperature dependent, varying essentially as $1/T$ and changing by two orders of

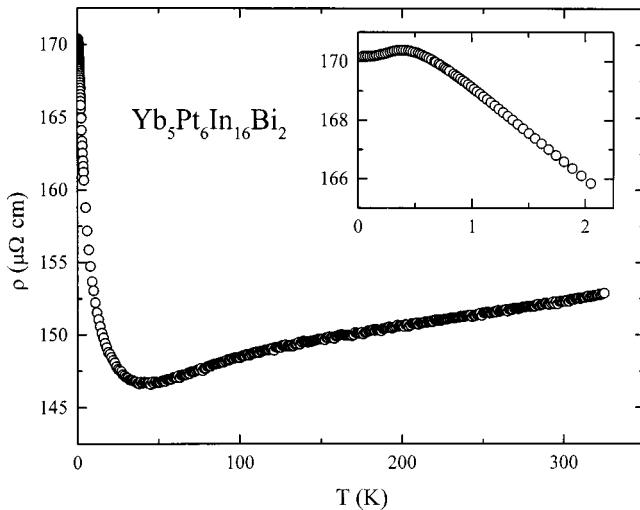
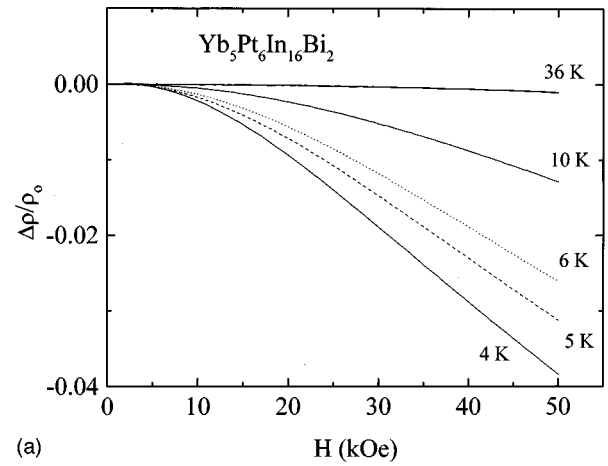
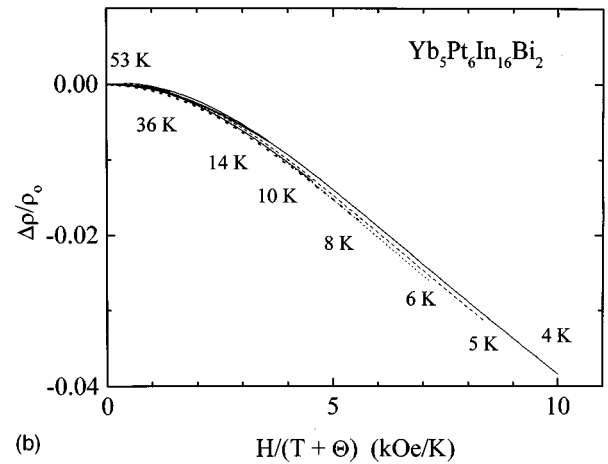


FIG. 6. Resistivity as a function of temperature. $\rho(T)$ below 2 K is shown in the inset.



(a)



(b)

FIG. 7. (a) Magnetoresistance isotherms in fields to 50 kOe. (b) Magnetoresistance field sweeps plotted as a function of $H/(T + \theta)$ with $\theta = 1$ K.

magnitude between 296 and 3 K. Although quantitative analysis is difficult because we cannot make a reasonable estimate of the non-magnetic scattering in the absence of a nonmagnetic analogue for $\text{Yb}_5\text{Pt}_6\text{In}_{16}\text{Bi}_2$, the Hall coefficient

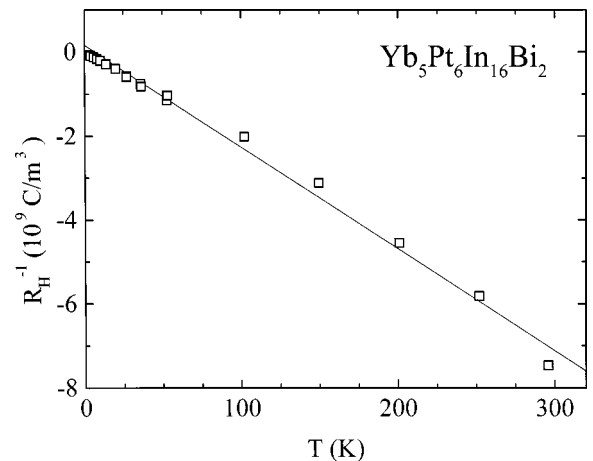


FIG. 8. Temperature-dependent 10 kOe Hall coefficient from 3 to 300 K plotted as R_H^{-1} versus T . The solid line is proportional to T , suggesting that the Hall coefficient is dominated by skew scattering.

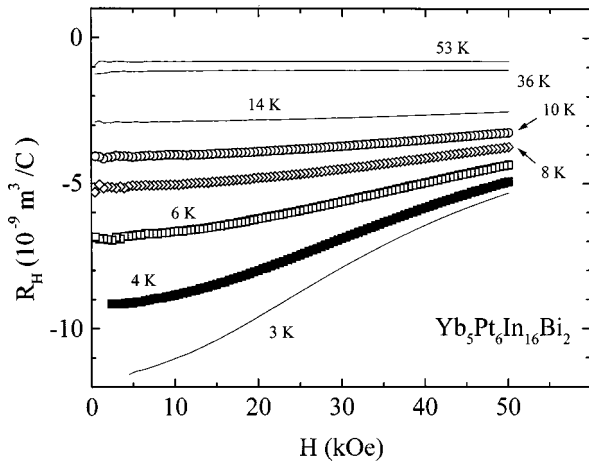


FIG. 9. Field-dependent Hall coefficient from 3 to 53 K.

data are consistent with a simple model consisting of a small T -independent conventional Hall term plus a larger skew-scattering contribution that follows the temperature dependence of the magnetic susceptibility (i.e., $\propto 1/T$).¹⁴ The field-dependent Hall coefficient is shown in Fig. 9. Similar to the magnetoresistance data, $R_H(H)$ is field-dependent at low temperatures and is essentially field-independent above 36 K.

Finally, the temperature-dependent thermoelectric power (TEP) is depicted in Fig. 10. The TEP is positive and exhibits a broad double-peak below 100 K and increases monotonically above 100 K, achieving a value of $2 \mu\text{V/K}$ at room temperature. As with the Hall-effect data, the overall magnitude of the TEP is characteristic of a metal, and the sign of thermoelectric power is consistent with an estimate of the non-skew-scattering contribution to the Hall effect (although R_H is large and negative, we estimate the ordinary Hall contribution to be small and positive).¹⁴ Given the degree of disorder present in this compound, it is unlikely that the broad maximum below 100 K arises from phonon drag. Rather, the peak in this temperature range is consistent with the crystal-field level scheme derived from the specific heat data. A semiphenomenological description¹⁵ of the TEP of Kondo compounds indicates that crystal-field effects produce

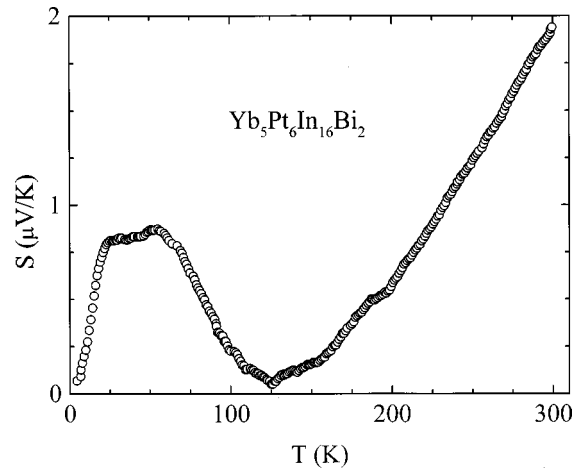


FIG. 10. Temperature-dependent thermoelectric power from 4 to 300 K.

broad maxima centered at roughly one-third of the energy splitting. Hence, the peak in thermopower centered at 25 K is consistent with the 60 K crystal-field levels(s) deduced from the specific heat data, and the second peak centered at roughly 60 K could arise from an additional, higher-energy crystal-field level.

SUMMARY

We have found that a quaternary compound with the approximate chemical composition $\text{Yb}_5\text{Pt}_6\text{In}_{16}\text{Bi}_2$ is closely related structurally to the stannide phase $\text{Tb}_5\text{Rh}_6\text{Sn}_{18}$. The compound appears to have inequivalent sites occupied by both divalent and trivalent Yb ions, displays chemical disorder similar to its stannide analogue, and undergoes a spin-glass transition near 300 mK. There is evidence from both thermodynamic and transport measurements of effects attributable to a crystal-field splitting of the trivalent Yb $J = 7/2$ Hund's rule ground state.

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