YbPtGe₂: A multivalent charge-ordered system with an unusual spin pseudogap

Roman Gumeniuk,^{1,*} Rajib Sarkar,¹ Christoph Geibel,¹ Walter Schnelle,¹ Carsten Paulmann,² Michael Baenitz,¹ Alexander A. Tsirlin,¹ Violeta Guritanu,¹ Jörg Sichelschmidt,¹ Yuri Grin,¹ and Andreas Leithe-Jasper¹

¹Max Planck Institute for Chemical Physics of Solids, Nöthnitzer Str. 40, 01187 Dresden, Germany

²DESY/HASYLAB, Notke Str. 85, 22603 Hamburg, Germany

(Received 2 November 2012; published 21 December 2012)

We performed a study of the structural and physical properties of YbPtGe₂. This compound is a multivalent charge-ordered system presenting an unusual spin pseudogap below 200 K. The crystal structure of YbPtGe₂ is refined from single-crystal and powder high-resolution synchrotron x-ray diffraction data at different temperatures. Analysis of the structural features of YbPtGe₂, together with a combined study of Yb *L*_{III} x-ray absorption spectroscopy, magnetic susceptibility $\chi(T)$, thermopower $S(T)$, and ¹⁷¹Yb and ¹⁹⁵Pt NMR indicate half of the Yb atoms to be in an intermediate valence state with an electronic configuration close to $4f^{13}$ (Yb³⁺), while for the remaining Yb atoms the $4f^{14}$ (Yb²⁺) configuration with almost no valence fluctuations is most likely. A drastic drop of the magnetic susceptibility and a decrease of the isotropic shift ¹⁹⁵K_{iso}(*T*) with decreasing temperature in the temperature range of 50–200 K evidence the opening of a spin pseudogap with an activation energy of $\Delta/k_B \sim 200$ K. Surprisingly, transport properties do not show clear evidence for the opening of a charge gap, thus excluding a standard Kondo-insulator scenario. Possible origins for this unusual electronic (valence) behavior are discussed.

DOI: 10.1103/PhysRevB.86.235138

PACS number(s): 75.30.Mb, 76.60.-k, 72.15.Eb, 75.20.Hr

I. INTRODUCTION

Electronic correlation effects observed in compounds formed by transition metals carrying itinerant *d* electrons and rare-earth (*RE*) metals with more localized *f* electrons is one of the central topics in solid-state chemistry and physics. These effects give rise to unusual behaviors, such as mixed and intermediate valence states, heavy fermion and non-Fermi liquid behaviors, superconductivity, Kondo insulators, Kondo semiconductors, quantum criticality, etc.^{1–4} Among the properties listed above, the heavy-fermion semiconductors, or alternately, Kondo insulators, attracted much attention in recent years. These materials exhibit a small gap at the Fermi level, which is believed to appear due to the hybridization between localized *d* or *f* electrons with conduction electrons¹ and thus is called a hybridization gap. Kondo insulators are characterized by an insulating or semiconducting electrical resistivity, a paramagnetic ground state with a pronounced drop in $\chi(T)$ towards low temperatures, and a mixed or intermediate valence state for the *f* element. The best-known examples of such materials are YbB₁₂ (Refs. 5–7), Ce₃Bi₄Pt₃ (Refs. 8 and 9), and FeSi (Refs. 2 and 10), etc. However, there are also Kondo insulators with a metallic type of electrical resistivity at the low temperatures, because the gap is filled with a low density of states, as, e.g., in the first proposed Kondo insulator CeNiSn.¹¹

Another interesting phenomenon of strongly correlated systems containing Yb is the occurrence of intermediate valence states where all Yb atoms present the same, nonintegral valence. In contrast, some compounds present a multivalent charge-ordered state where Yb atom on different sites show different electronic configurations. Such a valence state of Yb atoms has been reported for Yb₂Pt₃Sn₅ (Yb ions in one site are divalent and those in the other site are in a fluctuating state with valence close to +3)¹² and YbPd₃S₄ (divalent and trivalent Yb ions randomly occupy the 2a site with the appropriate ratio of Yb²⁺:Yb³⁺ = 2:3 or 4:1).^{13,14}

The recently discovered family of filled skutterudites MPt₄Ge₁₂ comprise several members [*M* = Sr, Ba (Refs. 15 and 16), La, Pr (Ref. 15), and Th (Refs. 17 and 18)] which become superconductors with *T*_c up to 8.3 K. CePt₄Ge₁₂ skutterudite was shown to be at the border of a typical intermediate valence state and a true Kondo-lattice behavior,^{19,20} while SmPt₄Ge₁₂ is a compound with an intermediate valence state of Sm atoms and exotic heavy-fermion behavior.²¹ Our attempts to synthesize skutterudites with [Pt₄Ge₁₂] framework with the heavier rare-earth metals failed. Instead, we found that compounds with a stoichiometry *M*₃Pt₄Ge₁₃ (*M* = Ca, Yb) form.²² Surprisingly, Yb atoms in Yb₃Pt₄Ge₁₃ show almost pure $4f^{14}$ (Yb²⁺) electronic configuration, which is the same valence, as reported for Eu species in the EuPt₄Ge₁₂ skutterudite.²³ In order to gain a deeper understanding of all exciting properties found for these compounds with high Ge content, we decided to investigate the valence state of Yb in YbPtGe₂, which is one of the precursors, together with elemental Ge and PtGe₂ used for the formation of the high-pressure Yb₃Pt₄Ge₁₃ phase.²²

REPtGe₂ compounds were an object of extended studies in the recent years. CePtGe₂ is reported to order ferromagnetically at *T*₀ = 3.7 K with a following metamagnetic spin-flip (or -flop) phase transition at lower temperatures.²⁴ The latest study²⁵ shows that CePtGe₂ orders ferromagnetically at *T*_c = 5.1 K. SmPtGe₂ shows a metallic type of conductivity and a 3+ oxidation state for samarium.²⁶ A neutron diffraction study revealed antiferromagnetic ordering for TbPtGe₂ at *T*_N = 24.2 K, with a change of propagation vector at lower temperatures.^{27–29} Magnetic properties and magnetic structures for REPtGe₂ (where *RE* = Gd–Er) are reported in Ref. 30. YbPtGe₂ has been reported to crystallize with the YIrGe₂ type (space group *Immm*, *a* = 4.37 Å, *b* = 8.734 Å, *c* = 16.134 Å) for the first time in Ref. 31 and later confirmed in Ref. 32. However, in both publications no crystal structure refinement for this compound was performed.

In this paper we report about the crystal structure and thermal expansion of YbPtGe_2 , which were studied using high-resolution synchrotron single-crystal and powder diffraction methods. Also, extended studies of physical properties of YbPtGe_2 , such as x-ray absorption spectroscopy (XAS), magnetic susceptibility, electrical resistivity, thermopower, thermal conductivity, ^{195}Pt and ^{171}Yb NMR, as well as reflectivity spectra were performed, and led us to conclude that Yb in this compound is in a multivalent charge-ordered state with an unusual spin pseudogap.

II. EXPERIMENTAL

A. Sample preparation

Samples with nominal composition YbPtGe_2 were prepared from ingots of ytterbium (Ames, 99.95 wt %), platinum foil (Chempur, 99.95 wt %), and semiconductor-grade germanium (Chempur 99.9999 wt %). The starting components were melted in glassy carbon crucibles under a purified argon atmosphere using a high-frequency furnace. The total mass of each sample was about 1 g, and mass losses after the melting procedure were not larger than 0.5%. The obtained buttons were placed in carbon crucibles, sealed in tantalum tubes, and enclosed in evacuated silica ampoules. The heat treatment was performed at 950 °C for 240 h with subsequent quenching in cold water. After such synthesis the obtained samples were very porous. Their compaction was carried out by spark plasma sintering in a SPS-515 ET/M apparatus (Dr. Sinter Lab) inside an argon-filled glove box. Typically 300 mg of the powder was loaded under argon into a WC/Co die with diameter of 6 mm. A solid pellet of equal dimensions and height of 1.4 mm was pressed by applying 600 MPa pressure. It was heated from 20 °C to 950 °C for 45 min and held at this temperature for 120 min. The obtained YbPtGe_2 pellets were mechanically robust and stable in air for a long time. To synthesize single crystals with a size suitable for an x-ray diffraction experiment, one of the annealed samples was heated to 1100 °C and cooled down to 950 °C within two weeks. All manipulations were performed inside an argon-filled glove box [$p(\text{O}_2/\text{H}_2\text{O}) \leq 1$ ppm]. Also the annealed samples are stable in air.

B. X-ray diffraction

Powder x-ray diffraction (XRD) of the samples was performed on a HUBER G670 imaging plate Guinier camera ($\text{Cu } K_{\alpha 1}$ radiation, $\lambda = 1.54056 \text{ \AA}$). The WINXPOW program package³³ was used for phase analysis. High-resolution XRD data for structure refinement were collected in the temperature range of 10–293 K at the ID31 beamline of the ESRF ($\lambda = 0.39993 \text{ \AA}$) on powder of YbPtGe_2 placed in a quartz capillary with an external diameter of 0.5 mm. The diffraction intensities were measured by eight scintillation detectors, each preceded by a Si(111) analyzer crystal, in the angle range $1^\circ \leq 2\theta \leq 40^\circ$. Cooling of the sample down to 10 K was carried out by a He-flow cryostat. The lattice parameters refinement by least-squares fitting as well as Rietveld refinements have been done using the program package WINCSD.³⁴

High-resolution single-crystal x-ray diffraction data were collected on crystals mechanically extracted from the sample

after synthesis (as described above) at beamline F1 (equipped with a κ -axis four-circle Huber diffractometer and a MAR165 CCD detector) at the HASYLAB/DESY, Hamburg, Germany. Temperatures of 100, 150, and 200 K for the experiment were maintained with an Oxford nitrogen gas-stream cooling device. Four shells of reciprocal space were covered with the CCD detector by $0.5^\circ \varphi$ rotations at goniometer angles 2θ , ω , χ , positioned at $(0^\circ, 0^\circ, 0^\circ)$; $(-60^\circ, 0^\circ, 0^\circ)$; and $(-60^\circ, 20^\circ, 60^\circ)$. Exposure times for runs at $2\theta = 0^\circ$ were 30 s, while for the high 2θ setting 90-s runs were chosen. The integration, data reduction, and scaling of measured intensities were performed using the XDS package, version 2009.³⁵ After that, intensities were corrected for the oblique incidence of x rays on the detector surface.^{36,37} Empirical absorption correction was carried out using the WINGX program.³⁸ Further details on the single-crystal data collection are given in Table I. Crystal structure of YbPtGe_2 at all temperatures has been refined using the program package WINCSD.³⁴

C. Metallography

Pieces of the annealed samples for the metallographic study were embedded in conductive resin and then ground, polished, and finished (1/4- μm diamond abrasives). Diamond suspension and appropriate lubricants suitable for moisture-sensitive materials were used during the microstructure preparation. The microstructure was investigated by light-optical microscopy (Zeiss Axioplan 2) and scanning electron microscopy (SEM; FEI Philips XL30). Energy-dispersive x-ray spectroscopical analysis (EDXS) was performed with the Si(Li)-detector of the EDXS system (Ametek, Genesis version 4.6) attached to the SEM. The spectra were recorded at acceleration voltages of 25 keV with a LaB_6 cathode. The chemical composition is calculated from the intensities of the Yb L , Pt L , and Ge K lines. The intensities were measured with a relative accuracy, providing a systematic inaccuracy of 0.5 at % for the content of each element. Four YbPtGe_2 samples were investigated metallographically. All of them were found to be single phase with the composition of $\text{Yb}_{1.00(1)}\text{Pt}_{1.00(1)}\text{Ge}_{2.00(1)}$.

D. Physical properties

Differential scanning calorimetry (DSC) was performed using an STA 409C NETZSCH device (Al_2O_3 crucibles, sample mass ~ 100 mg) under dynamic argon atmosphere in the temperature range of 30 °C–1200 °C with heating rates of 2 °C/min. The calibration was done using five melting standards (thermocouple type S). A strong peak observed at 992 °C in the heating curve indicates the congruent melting of YbPtGe_2 . This finding explains also the growth of crystals from the self-flux.

X-ray absorption near-edge spectroscopy (XANES) at the Yb L_{III} edge (8944 eV) was used to determine the temperature dependence of the Yb electronic state in the temperature range of 5–300 K. The XANES were recorded at the EXAFS beamline C of HASYLAB at DESY using the four-crystal mode of the Si(111) monochromator. In the helium-flow cryostat (Optistat CF, Oxford) the temperature was stabilized to better than $\Delta T < 0.1$ K. All spectra were determined in transmission mode using powdered samples (ca. 15 mg) which

TABLE I. Crystallographic data for YbPtGe₂ at different temperatures (structure type YIrGe₂, space group *Immm*, *Z* = 4).

Temperature Data	100 K	150 K single crystal	200 K	<i>RT</i> powder
Lattice parameters ^a				
<i>a</i> (Å)	4.33057(4)	4.33200(4)	4.33371(4)	4.33715(2)
<i>b</i> (Å)	8.73477(7)	8.73401(7)	8.73389(7)	8.73518(3)
<i>c</i> (Å)	16.1060(2)	16.1147(2)	16.1253(2)	16.14684(6)
<i>V</i> (Å ³)	609.2(1)	609.7(1)	610.4(1)	611.7(1)
ρ (g cm ⁻³)	11.18(1)	11.17(1)	11.16(1)	11.15(1)
Crystal size, mm	0.01 × 0.02 × 0.04	0.01 × 0.02 × 0.04	0.02 × 0.03 × 0.06	—
Diffraction system		F1, Hasylab		ID31, ESRF
Synchrotron radiation, λ (Å)		0.5		0.39993
$2\theta_{\max}$ (°)		106		45
Minimum <i>h, k, l</i>	−10, −28, −38	−10, −28, −38	−14, −15, −30	—
Maximum <i>h, k, l</i>	12, 22, 47	12, 22, 48	14, 28, 27	—
<i>N(hkl)</i> _{measured}	22307	22040	21477	—
<i>N(hkl)</i> _{unique}	5174	5113	4044	—
<i>N(hkl)</i> _{observed} [<i>F</i> _{<i>hkl</i>} ≥ 4σ(<i>F</i>)]	4872	4816	3814	—
<i>R</i> _{int} / <i>R</i> _{σ}	0.027/0.061	0.026/0.059	0.034/0.073	—
Refined parameters	39	39	39	26
Extinction coefficient	0.0063(2)	0.0066(2)	0.0035(2)	—
<i>R</i> _{<i>F</i>} / <i>wR</i> _{<i>F</i>²} or (<i>R</i> _{<i>B</i>})/ <i>R</i> _{<i>P</i>}	0.034/0.035	0.034/0.036	0.057/0.059	0.069/0.145
Yb ₁ in 4 <i>i</i> (0 0 <i>z</i>), <i>z</i>	0.20225(1)	0.20222(1)	0.20216(3)	0.20239(8)
<i>B</i> _{eq/iso}	0.178(2)	0.244(2)	0.336(5)	0.59(3)
Yb ₂ in 4 <i>g</i> (0 <i>y</i> 0), <i>y</i>	0.24071(3)	0.24055(3)	0.24029(5)	0.2417(2)
<i>B</i> _{eq/iso}	0.254(2)	0.353(2)	0.479(6)	0.65(3)
Pt in 8 <i>l</i> (0 <i>y</i> <i>z</i>), <i>y</i>	0.25004(1)	0.25004(1)	0.25005(2)	0.2498(1)
<i>z</i>	0.35075(1)	0.35066(1)	0.35057(2)	0.35044(4)
<i>B</i> _{eq/iso}	0.160(1)	0.217(1)	0.307(3)	0.62(2)
Ge ₁ in 4 <i>j</i> ($\frac{1}{2}$ 0 <i>z</i>), <i>z</i>	0.07525(3)	0.07524(3)	0.07519(9)	0.0752(2)
<i>B</i> _{eq/iso}	0.233(5)	0.310(6)	0.42(2)	0.42(8)
Ge ₂ in 8 <i>m</i> (<i>x</i> 0 <i>z</i>) <i>x</i>	0.0214(2)	0.0245(2)	0.0252(3)	0.042(2)
<i>z</i>	0.42364(4)	0.42366(4)	0.4237(1)	0.4229(2)
<i>G</i>	0.49(1)	0.49(1)	0.49(1)	0.49(1)
<i>B</i> _{eq/iso}	0.201(5)	0.267(6)	0.39(2)	0.49(9)
Ge ₃ in 8 <i>l</i> (0 <i>y</i> <i>z</i>), <i>y</i>	0.35124(4)	0.35124(4)	0.35124(8)	0.3510(2)
<i>z</i>	0.19838(2)	0.19831(3)	0.19820(6)	0.1976(2)
<i>B</i> _{eq/iso}	0.196(4)	0.255(4)	0.347(9)	0.42(5)

^aPowder XRD data for all temperatures. Values in parentheses are the statistical inaccuracies of the fits.

were diluted with B₄C and embedded in paraffin wax. To obtain the Yb valence, the XAS spectra were analyzed by a least-squares fitting procedure with two Lorentzian and two arctan functions using the program XASWIN.³⁹

The magnetization of polycrystalline samples was measured in a commercial magnetometer system (MPMS XL-7, Quantum Design) in external fields between $\mu_0 H = 2$ mT and 7 T and temperatures of 1.8–400 K.

The electrical resistivity $\rho(T)$ of polycrystalline samples was measured between 1.8 and 300 K by a four-point ac method using a commercial system (PPMS, Quantum Design). Electrical contacts were made with silver-filled epoxy resin.

The Seebeck coefficient of the thermopower, the thermal conductivity, as well as the resistivity were determined simultaneously on the TTO option of a PPMS.

Heat capacity was determined by a relaxation-type method between 1.8 and 320 K on a PPMS. At low temperatures the specific heat was also measured in magnetic fields up to $\mu_0 H = 9$ T.

Field-sweep NMR measurements were carried out using the conventional pulsed NMR technique on the ¹⁹⁵Pt (nuclear spin *I* = 1/2 and gyromagnetic ratio $\gamma/2\pi = 9.1096$ MHz/T) nuclei in the temperature range of 4.2 K ≤ *T* ≤ 295 K at a fixed frequency of 45 MHz in powder samples. The powder was mixed with paraffin in a small quartz tube, subsequently heated up and shaken, and then cured to randomize the grain. Because of the high NMR frequency and the metallic state of the material, such a process is required to prevent the NMR signal reduction due to the finite skin depth. The 4*f* contribution ¹⁹⁵*K*_{4*f*}(*T*) to the ¹⁹⁵Pt shift has been determined with respect to the nonmagnetic reference compound YPtGe₂. The field sweep spectra are obtained by integration over the spin echo in the time domain at a given field. The powder spectra are fitted with an anisotropic shift tensor. Shift components for *a*, *b*, and *c* directions are determined from the fitting of the spectra. The ¹⁹⁵*K*_{iso} has been calculated from the relation ¹⁹⁵*K*_{iso} = 1/3(*K*_{*a*} + *K*_{*b*} + *K*_{*c*}). Furthermore, the first preliminary ¹⁷¹Yb (*I* = 1/2) field-sweep NMR measurements

at 4.2 K are performed at various frequencies (15, 44, and 67 MHz).⁴⁰

Optical reflectivity measurements have been performed on polycrystalline YbPtGe₂ using a Fourier transform spectrometer (Bruker IFS 66 v/S) in the frequency range from 6.2 to 80 meV for different temperatures from 5 to 260 K. Absolute values of the reflectivity were calibrated against a reference gold layer evaporated *in situ* on the sample surface.

III. RESULTS AND DISCUSSION

A. Crystal structure

All peaks in the powder XRD pattern of YbPtGe₂ measured at room temperature were successfully indexed assuming an orthorhombic body-centered space group with the lattice parameters presented in Table I. Neither additional reflections nor any kind of splitting which could indicate the change of symmetry were found (see Fig. 1). The same situation is observed in the XRD patterns in the whole studied temperature range (20–300 K). Relative thermal expansion in all directions, which was deduced from the refinement of lattice parameters, is shown in Fig. 2. The change of lattice volume of YbPtGe₂ by 0.5% is typical for intermetallic compounds.^{41,42} However, as one can see from Fig. 2, this total thermal expansion is only due to the enlargement of the unit cell in the *a* and *c* directions. Unexpectedly, almost no expansion or even a small negative one is observed in the temperature range of 120–250 K along the *b* direction. A small negative volume thermal expansion is often observed for the Yb-based Kondo lattice or intermediate valence systems, but the present very anisotropic behavior is quite peculiar. To take a closer look at the change of the crystal structure we performed single-crystal x-ray diffraction experiments as a function of *T*.

Crystallographic data and details of the single-crystal data collection for YbPtGe₂ are listed in Table I. The starting model for the refinement was obtained applying direct methods. We observed a strong, unphysical difference in the isotropic displacement parameters for different Ge sites: $B_{eq} = 0.233(5)$ Å² for Ge₁ in 4*j*, $B_{eq} = 0.499(8)$ Å² for Ge₂ in 4*i*, and $B_{eq} = 0.196(4)$ Å² for Ge₃ in 8*l*. Furthermore, the displacement for Ge₂ occupying the 4*i* site is strongly anisotropic [$B_{11} =$

FIG. 1. (Color online) Room-temperature powder XRD pattern of YbPtGe₂.

FIG. 2. (Color online) Relative expansion of YbPtGe₂ calculated as $\eta_L = \frac{L(T) - L(20)}{L(20)} 100\%$, where the $L(T)$ are the cell parameters at the corresponding temperature *T*. The solid lines are guides for the eyes only.

1.11(2) Å², $B_{22} = 0.153(8)$ Å², $B_{33} = 0.23(1)$ Å²], which is typical for a split position. Therefore, the coordinate *x* for Ge₂ was set free in the further step of refinement. This changes the crystallographic site from 4*i* to 8*m*, and the occupancy factor *G* for the latter to 0.5 accordingly. Refinement performed in such a way leads to reasonable displacement parameters for all Ge atoms in the crystal structure of YbPtGe₂. The same structural model was then used for the Rietveld refinement of powder data at room temperature. Final atomic coordinates and displacement parameters at different temperatures for YbPtGe₂ are presented in Table I and anisotropic displacement parameters are listed in Table II. Interatomic distances in the crystal structure of YbPtGe₂ at different temperatures are listed in Table III.

The relationship of the YIrGe₂ structure with BaAl₄,⁴³ CeNiSi₂,⁴⁴ and ScRhSi₂ (Ref. 45) types have been discussed elsewhere.^{46,47} Here we would just like to note that the nearest coordination environment of the Yb₁ in the 4*i* crystallographic position consists of 4 Pt and 6 Ge atoms in form of a pentagonal prism, while that of Yb₂ in 4*g* is a hexagonal prism with 4 Pt and 8 Ge atoms, respectively (see Fig. 3).

The crystal structure of YbPtGe₂ can be considered as consisting of a Pt-Ge three dimensional framework, where Yb atoms are embedded. Fragments consisting of planar hexagonal rings connected with each other by a Ge₂-Ge₂ edge, and with pentagonal rings by Pt-Ge₁ edges, extend along the *b* direction. While the shortest Yb-Pt distances for Yb₁ and Yb₂ positions are close, the shortest Yb-Ge contacts increase drastically from 2.98 Å to 3.24–3.30 Å for Yb₁ and Yb₂, respectively. Such a situation with interatomic distances in YbPtGe₂ suggests different electronic states for Yb₁ and Yb₂ atoms in the crystal structure. Moreover, from this point of view, Yb₁ with a coordination polyhedron with smaller volume should show an electronic configuration closer to 4*f*¹³ (Yb³⁺), while Yb₂ with hexagonal prismatic coordination and larger volume is expected to possess configuration 4*f*¹⁴ (Yb²⁺).

Such a scenario suggests YbPtGe₂ to be rather similar to Yb₂Pt₃Sn₅ or YbPd₃Sn₄. The shortest Ge-Ge and Pt-Ge contacts in the crystal structure of YbPtGe₂ are shrunk by

TABLE II. Anisotropic displacement parameters for YbPtGe₂ at different temperatures.^{a,b}

Atom	B_{11}			B_{22}			B_{33}			B_{23}		
	100 K	150 K	200 K	100 K	150 K	200 K	100 K	150 K	200 K	100 K	150 K	200 K
Yb ₁	0.202(4)	0.266(4)	0.280(6)	0.146(3)	0.204(3)	0.253(6)	0.185(3)	0.260(4)	0.47(2)	0	0	0
Yb ₂	0.272(4)	0.367(4)	0.434(7)	0.262(3)	0.377(4)	0.465(7)	0.229(4)	0.316(4)	0.54(2)	0	0	0
Pt	0.194(3)	0.254(3)	0.276(4)	0.116(2)	0.164(2)	0.198(4)	0.169(2)	0.233(2)	0.447(8)	-0.005(1)	-0.006(2)	-0.008(3)
Ge ₁	0.39(1)	0.53(1)	0.64(2)	0.160(7)	0.209(8)	0.24(2)	0.151(8)	0.191(9)	0.38(4)	0	0	0
Ge ₃	0.197(7)	0.242(7)	0.26(1)	0.162(5)	0.215(5)	0.24(1)	0.229(6)	0.309(6)	0.54(3)	-0.021(4)	-0.038(5)	-0.05(1)

^a $B_{12} = B_{13} = 0$;^b B_{iso} was not refined for the Ge₂ split position.

1.5% and 5.7%, respectively, compared to the sum of atomic radii of the elements ($r_{\text{Yb}} = 1.94 \text{ \AA}$; $r_{\text{Pt}} = 1.38 \text{ \AA}$; $r_{\text{Ge}} = 1.23 \text{ \AA}$).⁴⁸ No short Pt-Pt contacts are observed. A closer look at Table III reveals also that many interatomic distances in the crystal structure of YbPtGe₂ (e.g., Yb₁-Ge₁, Yb₁-Pt, Pt-Ge₃, Ge₂-Ge₂, etc.) do not change between 100 and 200 K, and Yb₂-Ge₁ contact becomes even shorter. However, not all of them extend along the b direction, which makes it difficult to establish a correlation between a particular bond and the anomalous expansion along the b direction.

B. X-ray absorption spectroscopy (XAS)

The x-ray absorption spectra of YbPtGe₂ near the Yb L_{III} edge (Fig. 4) measured at different temperatures show two maxima. The maximum at higher energy (8942 eV) is nearly coincident with the spectrum of Yb₂O₃ oxide, reflecting the contribution of Yb with the $4f^{13}$ (Yb⁺³) configuration, while the shoulder at lower energy (8936 eV) indicates the presence of Yb⁺² species with the electron configuration $4f^{14}$. The ratio of intensities of both maxima are temperature dependent, which implies some intermediate valent character. Deconvolution of XAS spectra shows that the mean valence ν of Yb increases from +2.52(1) to +2.58(1) with increasing temperature. Similar small changes of the valence have been reported for many Yb-containing intermediate valence compounds: e.g., YbAl₃,^{49,50} YbCu₂Si₂,^{50,51} Yb _{x} In_{1- x} Cu₂,⁵² YbB₁₂,⁵ etc.

TABLE III. Interatomic distances d (Å) in the crystal structure of YbPtGe₂ at different temperatures.

Contact	100 K	150 K	200 K	RT
Yb ₁ -2Ge ₁	2.9787(4)	2.9797(4)	2.981(1)	2.987(2)
Yb ₁ -4Pt	3.1913(1)	3.1912(1)	3.1912(2)	3.1951(8)
Yb ₁ -2Yb ₂	3.8770(2)	3.8772(2)	3.8770(5)	3.890(1)
Yb ₂ -4Pt	3.2363(1)	3.2389(1)	3.2417(3)	3.2466(5)
Yb ₂ -4Ge ₁	3.2524(3)	3.2519(3)	3.2510(6)	3.261(2)
Pt-2Ge ₃	2.4691(2)	2.4691(2)	2.4690(4)	2.466(1)
Ge ₁ -1Ge ₁	2.4238(8)	2.4247(8)	2.425(2)	2.429(4)
Ge ₁ -2Pt	2.4876(3)	2.4885(3)	2.4899(7)	2.494(2)
Ge ₂ -1Ge ₂	0.186(1)	0.212(1)	0.219(2)	0.367(9)
Ge ₂ -1Ge ₂	2.4599(9)	2.461(1)	2.460(2)	2.491(5)
Ge ₂ -2Pt	2.4812(4)	2.4828(4)	2.4846(9)	2.482(2)
Ge ₂ -2Yb ₂	3.3072(6)	3.3003(6)	3.300(1)	3.253(4)
Ge ₃ -1Ge ₃	2.5989(5)	2.5987(5)	2.599(1)	2.603(3)
Ge ₃ -2Yb ₁	2.9898(3)	2.9916(3)	2.9943(7)	3.001(2)

C. Magnetic susceptibility

The temperature dependence of the magnetic susceptibility $\chi(T)$ of YbPtGe₂ is shown in Fig. 5. In the temperature range of 400–800 K it may be described by a Curie-Weiss (CW) law [$\chi = C/(T + \theta)$] (right inset in Fig. 5). The effective magnetic moment μ_{eff} and the Weiss temperature θ_P determined above 400 K from a linear fit to $1/\chi$ are $3.31 \mu_B$ and 435 K, respectively. The obtained θ_P is related to the large characteristic energy (250 K) of the valence fluctuations of the system (see below). Since the value of μ_{eff} is close to $1/\sqrt{2}$ of the effective moment of trivalent Yb [$\mu_{\text{eff}}(\text{Yb}) = 4.54 \mu_B$; $1/\sqrt{2}\mu_{\text{eff}}(\text{Yb}) = 3.21 \mu_B$], it strongly suggests that one of the Yb sites (likely Yb₁) is close to trivalent, while the other site is occupied by divalent Yb.

Below 400 K, the magnetic susceptibility of YbPtGe₂ deviates drastically from the Curie-Weiss fit and shows a broad maximum at about 250 K followed by a pronounced decrease by almost a factor of 2, down to 20 K. While the maximum around 200 K is very typical of an intermediate valence system with a valence not too far from $3+$, such as, e.g., YbAl₃,⁵³

FIG. 3. (Color online) Coordination polyhedra of Yb atoms in the crystal structure of the YbPtGe₂ compound (dark gray: Yb₁ in $4i$; light gray: Yb in $4g$; red: Pt atoms; blue: Ge).

FIG. 4. (Color online) Yb L_{III} x-ray absorption spectra of YbPtGe₂ at different temperatures together with reference spectrum of Yb₂O₃. Inset: Development of the mean Yb valence ν as a function of temperature. Red line is a guide for the eyes.

the drop below 200 K is much more pronounced; usually in intermediate valence systems the decrease in $\chi(T)$ is only of the order 10%–20%. This significant drop thus evidences the opening of a spin gap in YbPtGe₂. In order to analyze $\chi(T)$ further, we tried a fit with the interconfiguration fluctuation (ICF) model.⁵⁴ The fit presented in Fig. 5 (blue dashed line) has been carried out in the temperature range of 50–800 K according to the formula^{54–56}

$$\chi(T) = \frac{1}{2} \chi_{ICF}(T) + \chi_{imp}(T) + \chi_0(T), \quad (1)$$

where $\chi_{ICF}(T) = N_A \mu_{eff}^2 [1 - \nu_{ICF}] / k_B (T + T_{sf})$ is the susceptibility given by the ICF model (here reduced by a factor of 2, since only one half of Yb atoms in the crystal structure shows valence fluctuations) with fractional occupation of the divalent state $\nu_{ICF}(T) = 1 / \{1 + 8 \exp[-E_{ex}/k_B (T + T_{sf})]\}$ (E_{ex} is the interconfigurational excitation energy and T_{sf} defines a width of all sublevels of two configurations);

FIG. 5. (Color online) Magnetic susceptibility $\chi(T)$ of YbPtGe₂ together with the ICF fit and the prediction of the Coqblin-Schrieffer model of Rajan for $J = 7/2$ ($\chi_{sc} = 8.6 \times 10^{-4}$ emu mol⁻¹, $T_0 = 682$ K). Left inset: Dependencies of valence ν of Yb atoms vs temperature derived from XAS and ICF fit. Right inset: Inverse magnetic susceptibility $1/\chi(T)$ (scale begins with 0.3×10^{-3} mol emu⁻¹) together with Curie-Weiss fit.

$\chi_{imp}(T) = C_{imp}/(T + \theta_{imp})$ is the Curie-Weiss impurity contribution at low temperatures (< 20 K); and χ_0 represents the contribution of conduction-electron paramagnetism.

The following values of the parameters were obtained: $E_{ex}/k_B = 763(2)$ K; $T_{sf} = 111(1)$ K; $C_{imp} = 0.03(1)$ emu K mol⁻¹; and $\theta_{imp} = -1.4(2)$ K, $\chi_0 = -4.3(2) \times 10^{-5}$ emu mol⁻¹. Assuming a purely divalent state on Yb₂, the average valence of the Yb atoms ($n = 5/2 - \nu/2$) in YbPtGe₂ deduced from these parameters is given in the left inset to Fig. 5. The absolute value of the ICF valence is well below that of the XAS experiment. This discrepancy can be removed by increasing the valence of the Yb₂ site. But, more importantly, the ICF model results in a much stronger decrease of the valence below 300 K than observed with XAS, since it mimics the pronounced decrease in $\chi(T)$ by a strong decrease in $\nu(T)$. This comparison shows that such decrease in $\chi(T)$ cannot be accounted for by the XAS-determined change of the mean valence of Yb atoms in YbPtGe₂.

The broad and large maximum in $\chi(T)$ is also a typical feature for a Kondo-lattice system with a large characteristic energy. The Coqblin-Schrieffer model of Rajan⁵⁷ describes well the properties of some RE impurities such as Ce ($J = 5/2$) and Yb ($J = 7/2$) in a metal, assuming that not only the crystal electric field (CEF) ground-state doublet is involved in the physics at low temperatures, but also some excited CEF states.

Comparison of normalized $\chi(T)/\chi_{sc}$ with the model of Rajan reveals a very good agreement with the theoretically calculated data for the whole multiplet $J = 7/2$ of Yb⁺³ (Fig. 5, red line) in the high-temperature range of 200–800 K. However, at lower temperatures the experimental susceptibility deviates drastically from the theoretically predicted curve.

The failure of the Kondo model to reproduce $\chi(T)$ and the failure of the ICF model to reproduce the mean valence determined directly by XAS is basically related to the pronounced decrease of $\chi(T)$, about a factor of 2, between 200 and 20 K. Such a decrease is much too large for a conventional metallic IV system. It suggests the opening of a spin pseudogap. Thus convoluting the Coqblin-Schrieffer susceptibility with an activated term according to the formula $\chi(T) = \chi_{cs}(T)[1 + w_g(\exp\{-\Delta/k_B T\}) - 1]$ [where $\chi_{cs}(T)$ is the Coqblin-Schrieffer model, w_g the gapped fraction of the valence fluctuating part, and Δ/k_B is the activation gap] results in a fit (not shown for clarity) of the same quality as the ICF model. In this fit the fractions of the gapped spin moments $w_g = 0.57(1)$ are close to 50% and $\Delta/k_B = 170$ K is in good agreement with the activation gap of 200 K obtained from the fit of $^{195}\text{K}_{iso}(T)$ (see Sec. H). Such a pseudogap is expected and has been observed for Kondo-insulator systems such as YbB₁₂,⁵⁸ Ce₃Pt₃Bi₄,⁸ and U₂Ru₂Sn.⁵⁹ They show very similar behavior of $\chi(T)$ as observed for YbPtGe₂. However, Kondo insulators are also characterized by a semiconducting type of temperature dependence of electrical resistivity,¹ which we do not observe for YbPtGe₂.

D. Electrical resistivity

Surprisingly, no signature of an energy gap is observed in the electrical resistivity of YbPtGe₂ (see Fig. 6). It behaves like a typical simple metallic system. For the temperature range 7–20 K the resistivity is fitted to $\rho_0 + A_{FL}T^2$ with a residual

FIG. 6. (Color online) Temperature dependence of electrical resistivity of YbPtGe₂. Inset shows a fit to the $\rho_0 + A_{FL}T^2$ relation in the temperature range 7–20 K (red line).

resistivity $\rho_0 = 9.66(1) \mu\Omega \text{ cm}$ from impurity scattering, and the cross section of the quasiparticle-quasiparticle scattering $A_{FL} = 8.4(1) \times 10^{-3} \mu\Omega \text{ cm K}^{-2}$. Below 7 K, there seems to be a small additional contribution (this might, e.g., originate from Yb on defect sites behaving as single Kondo ions) to $\rho(T)$, which results in a slight upward deviation from the T^2 behavior. The room-temperature resistivity $\rho(300 \text{ K})$ of YbPtGe₂ is $203 \mu\Omega \text{ cm}$, and taking into account the value of the residual resistivity, we find a residual resistivity ratio $\text{RRR} = 21$, indicating a fairly good quality of the investigated sample.

The Kadowaki-Woods ratio⁶⁰ $R_{KW} = A_{FL}/\gamma^2$ for YbPtGe₂ is $6.6 \times 10^{-5} \mu\Omega \text{ cm (mol K mJ}^{-1})^2$ is slightly larger than the order of magnitude expected for a Fermi liquid: $1.0 \times 10^{-5} \mu\Omega \text{ cm (mol K mJ}^{-1})^2$ and much larger (a factor of ~ 100) than the values reported for Yb-based intermediate-valence systems.⁶¹ This is likely due to grain boundaries/cracks in the sample that lead to the overestimation of the absolute value of $\rho(T)$.

E. Specific heat

The low-temperature specific heat for YbPtGe₂ in different magnetic fields is shown in Fig. 7 (in the inset it is presented in a c_p/T vs T^2 representation). A small anomaly at 2.3 K, corresponding to 0.5 mol. % of the antiferromagnetic Yb₂O₃ (Ref. 62) impurity, is observed. In the temperature range 2.6–10 K, $c_p(T)$ is described by $c_p(T) = \gamma T + \beta T^3 + \delta T^5$, where γ is the Sommerfeld coefficient of the electronic heat capacity, and β, δ are the first terms of the harmonic lattice approximation for the phonon contribution. A fit with this relation results in $\gamma = 11.3(1) \text{ mJ mol}^{-1} \text{ K}^{-2}$, $\beta = 0.72(1) \text{ mJ mol}^{-1} \text{ K}^{-4}$, which corresponds to an initial Debye temperature $\Theta_D(0) = 221(5) \text{ K}$, and $\delta = 1.25(1) \times 10^{-3} \text{ mJ mol}^{-1} \text{ K}^{-6}$.

The γ value is of the order of magnitude expected for intermediate-valence systems with such a valence and characteristic energy. It evidences a quite significant density of states at the Fermi level ($\approx 4.8 \text{ states eV}^{-1}$), which excludes the opening of a significant pseudogap in the charge excitations. From the T -independent part of the susceptibility at low temperatures, $\chi_0 \approx 1.0 \times 10^{-3} \text{ emu mol}^{-1}$, the

FIG. 7. (Color online) Specific heat for YbPtGe₂ in different magnetic fields at low temperatures. Inset: Specific heat in c_p/T vs T^2 representation ($\mu_0 H = 0 \text{ T}$) together with the fit to the $c_p(T) = \gamma T + \beta T^3 + \delta T^5$ equation (red solid line).

Sommerfeld coefficient γ , and taking μ_{eff} as determined from the high-temperature susceptibility, we calculated a Wilson ratio $R_W = \chi_0/\gamma\pi^2(k_B^2/\mu_{\text{eff}}^2) = 1.8$, which is a typical value for a valence fluctuating system. As expected for such a weakly magnetic system, magnetic field has no observable effect on the specific heat.

Since no phonon reference compound (i.e., LuPtGe₂) can be synthesized, the $4f$ contribution to $c_p(T)$ of YbPtGe₂ was not estimated. At room temperature the value of the specific heat (c_p) for YbPtGe₂ is $103 \text{ J mol}^{-1} \text{ K}^{-1}$, in good agreement with the Dulong-Petit law ($c_p = 3nR$; n = number of atoms/f.u.).

F. Thermopower

The temperature dependence of the thermopower $S(T)$ for YbPtGe₂ is shown in Fig. 8. It is negative in the whole measured temperature range (1.8–400 K), with a wide minimum of $-46 \mu\text{V K}^{-1}$ at $T_{\text{min}} = 195 \text{ K}$. Such behavior of $S(T)$ is characteristic for Yb-containing intermediate-valence

FIG. 8. (Color online) Temperature dependence of the Seebeck coefficient of the thermopower $S(T)$ of YbPtGe₂ (circles), together with a fit (line) to the data according to $S(T) = AT/(B^2 + T^2)$ in the temperature range $110 \text{ K} < T < 350 \text{ K}$.

compounds and is observed in YbAu₂In, YbCu₂Si₂,⁶³ as well as in the multivalent charge-ordered system Yb₂Pt₃Sn₅.¹²

A phenomenological model for the quasiparticle electronic density of state (DOS), N^{4f} , at the Fermi level could be used for the analysis of the thermopower of $4f$ systems at the border of the intermediate valence regime.⁶⁴ Within this theory $S(T)$ is given as

$$S = \frac{AT}{B^2 + T^2}, \quad (2)$$

with

$$A = \frac{2(\epsilon_0 - \epsilon_F)}{|e|}; \quad B^2 = 3 \frac{(\epsilon_0 - \epsilon_F)^2 + (\Delta)^2}{\pi^2 k_B^2}, \quad (3)$$

where ϵ_0 is the position of the renormalized $4f$ states with respect to the Fermi energy ϵ_F , $|e|$ is the charge of the electron, and Δ is the width of the Kondo resonance peak. For Yb-containing compounds, the center of the resonance ϵ_0 is situated below ϵ_F , yielding a negative slope of the DOS at ϵ_F , and thus negative values of the thermopower.

Assuming a Lorentzian shape for $N^{4f}(\epsilon)$, one can write

$$N^{4f}(\epsilon) = \frac{W}{\pi} \frac{\frac{1}{2}\Delta}{(\epsilon_0 - \epsilon)^2 + (\frac{1}{2}\Delta)^2}, \quad (4)$$

where W is the integrated weight, which can be approximated in the intermediate valence regime by $W = Q_z^+ + Q^-(1 - z)$, where for Yb $Q^+ = 8$, $Q^- = 1$, and $n_h = 1 - z$ is the number of holes in the $4f$ shell.⁶⁴ The Yb valence $\nu = 3 - z$ can be determined from the following condition:

$$n_h = 1 - z = \int_{\epsilon_F}^{\infty} N^{4f}(\epsilon) d\epsilon. \quad (5)$$

The experimental $S(T)$ for YbPtGe₂ was successfully fitted to Eq. (2) in the temperature range of 110–350 K (line in the Fig. 8). At lower temperatures the experimental curve deviates slightly from the fitted line due to the presence of additional scattering mechanisms. Parameters obtained from the fit were $A = -1.72 \times 10^4 \mu\text{V}$ and $B^2 = 3.61 \times 10^4 \text{K}^2$. The values for $\epsilon_0 - \epsilon_F$ and Δ calculated from Eq. (3) are -8.5 and 28.4 meV, respectively. They are of the same magnitude as reported for such known intermediate valence compounds as YbCu₂Si₂ (Ref. 63) and Yb₂Pt₃Sn₅.¹² From these parameters we calculated $z = 0.2$, which results in a valence of 2.8 for the Yb in the intermediate-valence state. This is as expected from the position of the extrema in $\chi(T)$ or $S(T)$, and in connection with the much smaller mean valence observed in the XAS spectra, giving further support for a multivalent charge-ordered system. *Nota bene*: In Kondo and IV systems the absolute values of the thermopower do not scale with the number of IV ions.

Thus, we conclude that this simple phenomenological approach explains satisfactorily the temperature dependence of the thermopower $S(T)$ for YbPtGe₂, which suggests a simple intermediate valence state for at least a part of the Yb atoms in the investigated compound.

On the other hand, for a Kondo insulator, such as, *e.g.*, YbB₁₂, with an energy gap of an order of 100 K, two minima in the temperature dependence of the thermopower $S(T)$: $S_{\min 1} =$

FIG. 9. (Color online) Temperature dependence of the thermal conductivity $\kappa(T)$ of YbPtGe₂, with its electronic (κ_{el}) and phonon (κ_{ph}) contributions.

$-125 \mu\text{V K}^{-1}$ at around $T_{\min} = 100$ K and $S_{\min 2} = -130 \mu\text{V K}^{-1}$ at around $T_{\min} = 10$ K, are observed.^{65,66}

G. Thermal conductivity

The temperature dependence of the thermal conductivity $\kappa(T)$ for YbPtGe₂ is shown in Fig. 9. With decreasing temperature, $\kappa(T)$ decreases to around 100 K and, with the further decrease of temperature, it passes through a broad maximum at $T_{\max} = 28$ K.

For metallic compounds $\kappa(T)$ can be decomposed into κ_{el} and κ_{ph} . The electronic contribution κ_{el} may be estimated from the experimental resistivity data by applying the Wiedemann-Franz law $\kappa_{\text{el}}(T) = L_0 T / \rho(T)$, where L_0 is the Lorenz number $2.44 \times 10^{-8} \text{W } \Omega \text{ K}^{-2}$. The calculated κ_{el} for YbPtGe₂ is depicted by the red line in Fig. 9. The phonon contribution κ_{ph} was estimated by subtracting κ_{el} from the measured value of κ , exhibiting a broad maximum at around 28 K.

The thermal conductivity $\kappa(T)$ of YbPtGe₂ is quite low compared to good metals or intermetallic compounds consisting only of rare-earth and $3d$ -transition metals.⁶⁷ On the other hand, it is of the same order of magnitude as those reported for the typical intermediate-valence compound CePd₃ (Ref. 68) or the heavy-fermion semiconductor CeNiSn.⁶⁹ Also for YbPtGe₂, similar to CePd₃ or CeNiSn, the heat conduction via phonons is dominating. Phonons are also mainly contributing to the thermal conductivity $\kappa(T)$ in Kondo insulators. In particular, it is the case for FeSi (Ref. 70) and YbB₁₂.⁶⁵ This can be understood on the basis that the electronic contribution to the thermal current is small due to the small value of the electronic DOS at the Fermi energy ϵ_F and a large electronic scattering rate.² However, absolute values of $\kappa(T)$ of these Kondo insulators are 1 order of magnitude smaller than those observed for the metallic conductor YbPtGe₂.

H. ¹⁹⁵Pt NMR

Detailed field sweep solid-state NMR investigations on the ¹⁹⁵Pt NMR nuclei were carried out. With a natural abundance of 100% and a nuclear spin of $J = 1/2$, Pt is a very suitable nuclei for probing the magnetism in YbPtGe₂. The NMR shift probes the local spin susceptibility, which is in contrast to

FIG. 10. (Color online) $^{195}\text{K}_{\text{iso}}(T)$ vs T plot at 45 MHz for YbPtGe₂ together with the activation gap fit. Inset shows the $^{195}\text{K}_{\text{iso}}$ vs χ plot.

the bulk susceptibility free from impurity contributions from residual foreign phases. Figure 10 shows the ^{195}Pt NMR shift ($^{195}\text{K}_{\text{iso}}$) of YbPtGe₂ at a fixed frequency of $\nu = 45$ MHz ($\mu_0^{195}H_L = 4.9398$ T) as a function of temperature. The shift is negative, as expected for a Yb-based compound according to the simple conduction electron polarization model. The isotropic shift $^{195}\text{K}_{\text{iso}}(T)$ is linear with the bulk susceptibility $\chi(T)$ (Fig. 5, inset) over a wide range in temperature. Below 30 K, where a small amount of paramagnetic impurity prevails in the bulk susceptibility (“Curie tail”), a deviation is observed. Here, in contrast to the bulk susceptibility, the residual shift becomes temperature independent. Towards higher temperatures shift and susceptibility exhibit a broad maximum and decrease again. This behavior is reminiscent to the Kondo insulators such as YbB₁₂ (Ref. 7) or Ce₃Bi₄Pt₃,⁷¹ where such a large increase is related to the opening of a gap or a pseudogap in the DOS at E_F . Therefore we have fitted $^{195}\text{K}_{\text{iso}}$ with a simple activation gap model using the equations $^{195}\text{K}_{\text{iso}} = K_{T \rightarrow 0} + A \exp(-\Delta/k_B T)$. This simulation gives a gap value of $\Delta/k_B \sim 200$ K. The inset of Fig. 10 shows the shift vs susceptibility plot. We obtain a hyperfine coupling constant $A_{\text{hf}} = 7.261$ kOe/ μ_B between 28 and 180 K and a temperature independent shift $K_{T \rightarrow 0} = -0.21\%$ at low temperature. At high temperature there is a change of slope in the K vs susceptibility plot, indicating the change of the hyperfine coupling constant.

To study the effect of this spin gap on the dynamical susceptibility, we also investigated the spin-lattice relaxation rate ($1/T_1$), which is related to the DOS at the Fermi level. Consequently, the opening of a gap should result in a drastic, exponential decrease of $1/T_1$ with decreasing temperature [$1/T_1 \sim \exp(-\Delta/k_B T)$]. However, we have not observed such drastic effect in measured $1/T_1$ values, except for a small change in the slope of the $1/T_1$ vs T plot. So the dependence of the spin-lattice relaxation rate does not support the Kondo insulator picture and confirms the absence of a significant pseudogap in the charge excitations. Fortunately there are other NMR active nuclei in the sample. Probing ^{171}Yb opens up the opportunity to do NMR on the magnetic ion directly. In the picture we propose there are two Yb sites hosting two different Yb species (see subsection magnetic susceptibility). One Yb

is rather magnetic and its valence is close to 3, whereas the other one is rather nonmagnetic with a valence close to 2. We have found the ^{171}Yb NMR line at 4.2 K around the Larmor field $\mu_0^{171}H_L = 3.20$ T at 24 MHz. Because of its small shift we speculate that this corresponds to the nonmagnetic Yb²⁺ species. Until now we could not find the NMR line of the magnetic Yb species, which is expected to be strongly shifted. However, it is questionable whether it is possible to find this line because ^{171}Yb NMR on the magnetic species Yb³⁺ is hard to find (see work on YbAl₂ and YbAl₃, Ref. 72). The NMR investigations on the ^{171}Yb nuclei as well as the relaxation measurements are still in progress and might be published elsewhere.⁴⁰

To conclude, the present NMR results confirm the intrinsic nature of the bulk susceptibility on a microscopic scale. While the temperature dependence of ^{195}Pt NMR shift is reminiscent of correlated semiconductors such as YbB₁₂ (Ref. 7) and indicate the opening of a spin pseudogap with a value of about $\Delta/k_B \sim 200$ K, the temperature dependence of spin-lattice relaxation $1/T_1$ shows no evidence for a pseudogap formation. Additionally, ^{171}Yb NMR provides evidence for the presence of a nonmagnetic Yb²⁺ line.

I. Reflectivity spectra

Figure 11 shows the reflectivity of YbPtGe₂ at selected temperatures. The increase of the reflectivity at low energies with decreasing temperature corresponds to the expected behavior for a metal, in agreement with the metallic response seen in the dc resistivity (see Fig. 6). However, in the energy range between 20 and 40 meV we observe a weak suppression of the reflectivity below 100 K (see inset), indicating a change of the electronic excitations around this temperature. A similar, but much more pronounced reflectivity suppression is typical for the optical spectra of intermediate-valence systems,⁷³ e.g., YbAl₃. The fact that in YbPtGe₂ such a feature is less marked

FIG. 11. (Color online) Near-normal incidence reflectivity spectra of polycrystalline YbPtGe₂ at 5, 50, 70, 100, 150, 200, and 260 K (from top to bottom). The arrow marks the frequency position where the suppression of $R(\omega)$ is the strongest. The weak structure seen at 47 meV is an experimental artifact. Inset: The temperature dependence of $R(\omega)$ at 25 meV (circles), 28 meV (squares), and 35 meV (triangles).

could be related to the multivalent charge-ordered state of Yb. Unfortunately, the reflectivity spectra above 60 meV were not reproducible in repetitive experiments, and therefore a more quantitative analysis was not possible. In contrast, the spectral shape below 60 meV is robust.

IV. CONCLUSIONS

The crystal structure of YbPtGe₂ was refined from single-crystal and powder high-resolution synchrotron XRD data. Different to the YIrGe₂ type, we found that one of the Ge positions breaks the symmetry of the space group *Immm* and is described by a split with occupational parameter *G* of 0.5. Interatomic distances in the crystal structure of YbPtGe₂, as well as different coordination of Yb atoms occupying two distinct crystallographic sites, suggest a $4f^{13}$ (Yb³⁺) electronic configuration for Yb₁, which is in closer contact with Ge and Pt (shortening of Yb-Ge and Yb-Pt distances by 6% and 4% compared with Yb₂, respectively), and a $4f^{14}$ (Yb²⁺) configuration for Yb₂ (no shortening of Yb-Ge contacts and shrinking of Yb-Pt distance by only 2.2%–2.5%). Thus, already from these structural peculiarities it can be inferred that YbPtGe₂ is a multivalent charge-ordered system.

Measurements of the thermal expansion in YbPtGe₂ reveal a strong anisotropy of this property. An increase of the unit cell along *a* and *c* directions was observed, while a negative expansion occurs in the *b* direction. The origin of the negative expansion along the *b* direction is not clear. The thermal expansion of the unit-cell volume of YbPtGe₂ between 5 and 293 K is calculated to be 0.5%, which is rather typical for intermetallics.

A deconvolution of Yb *L*_{III} XAS spectra shows that the mean valence *ν* of Yb increases from +2.52(1) to +2.58(1) between 4 and 293 K, thus clearly indicating the intermediate valence state of Yb species in YbPtGe₂. This finding is corroborated also by the temperature dependence of the thermopower *S*(*T*), which was successfully analyzed within a phenomenological model for the quasiparticle DOS, resulting in a Yb valence *ν* = 2.8, as well as by the rather small thermal conductivity. The broad maximum at 250 K observed in the temperature dependence of the magnetic susceptibility $\chi(T)$ of YbPtGe₂ also resembles the behavior of intermediate valence systems, but the temperature of the maximum $T_{\text{max}} \approx 250$ K indicates a valence above 2.8.⁷⁴ The origin of this discrepancy is revealed

by the effective magnetic moment, deduced from the CW fit of $\chi(T)$ above 300 K, which is close to $1/\sqrt{2}\mu_{\text{eff}}(\text{Yb}^{3+})$. In connection with the results of the structural investigation, this is a strong evidence that Yb₁ is in an IV state with a valence not far from 3+, while Yb₂ is in an IV state with a valence not far from 2+. The observation of the ¹⁷¹Yb NMR line with almost no shift is an additional microscopic evidence for such an assumption. Therefore, we conclude YbPtGe₂ to be a multivalent charge-ordered system, where Yb₁ atoms in the 4*i* site are in IV state with the electronic configuration close to the $4f^{13}$ (Yb³⁺), while Yb₂ atoms in the 4*g* site show $4f^{14}$ (Yb²⁺) configuration with almost no valence fluctuations.

The strong decrease of $\chi(T)$ of YbPtGe₂ below 200 K by 50% indicates the opening of a spin pseudogap. This is supported by the local probe ¹⁹⁵Pt NMR study. A sharp increase of the isotropic shift ¹⁹⁵*K*_{iso}(*T*) with increasing temperature indicates an activation energy of $\Delta/k_B \sim 200$ K.

However, electrical resistivity and specific heat measurements show YbPtGe₂ to be a good metal without any evidence for the opening of a pseudogap. Furthermore, the temperature dependence of the relaxation rate $1/T_1$ observed in the NMR experiment as well as the temperature dependence of the optical reflectivity show only weak changes, confirming the absence of a gap in the charge excitations. Therefore, the spin-gap cannot be attributed to the formation of a Kondo insulator or Kondo semimetallic state. This discrepancy between the clear evidence for the opening of a pseudogap in the spin excitations and its absence in the charge excitations is surprising. The investigation of its origin deserves further measurements on single crystals. It might be related to the anomalous thermal expansion observed along the *b* direction.

ACKNOWLEDGMENTS

The authors thank I. Veremchuk for performing spark plasma sintering on the samples, and C. Curfs for assistance during high-resolution XRD measurements at ID31. We are grateful to U. Burkhardt, P. Scheppan, and S. Kostmann for metallographical study on the samples, and H. Borrmann, Yu. Prots, and S. Hückmann for performing x-ray powder diffraction. The authors are deeply indebted to S. Hoffmann and S. Scharsach for performing DSC measurements, and L. Akselrud and H. Rosner for fruitful discussions.

*Roman.Gumeniuk@cpfs.mpg.de

¹D. Adroja, K. McEwen, J.-G. Park, A. Hillier, N. Takeda, P. Riseborough, and T. Takabatake, *J. Optoelectron. Adv. Mater.* **10**, 1719 (2008).

²P. Riseborough, *Adv. Phys.* **49**, 257 (2000).

³G. Stewart, *Rev. Mod. Phys.* **73**, 797 (2001).

⁴A. Georges, G. Kotliar, W. Krauth, and M. J. Rozenberg, *Rev. Mod. Phys.* **68**, 13 (1996).

⁵M. Kasaya, F. Iga, K. Negishi, S. Nakai, and T. Kasuya, *J. Magn. Magn. Mater.* **31–34**, 437 (1983).

⁶F. Iga, M. Kasaya, and T. Kasuya, *J. Magn. Magn. Mater.* **76–77**, 156 (1988).

⁷M. Kasaya, F. Iga, M. Takigawa, and T. Kasuya, *J. Magn. Magn. Mater.* **47–48**, 429 (1985).

⁸M. F. Hundley, P. C. Canfield, J. D. Thompson, Z. Fisk, and J. M. Lawrence, *Phys. Rev. B* **42**, 6842 (1990).

⁹M. Jaime, G. Stewart, W. Beyermann, M. Berisso, M. Hundley, P. Canfield, and J. Sarrao, *Nature (London)* **405**, 160 (2000).

¹⁰V. Jaccarino, G. K. Wertheim, J. H. Wernick, L. R. Walker, and S. Aarj, *Phys. Rev.* **160**, 476 (1967).

¹¹T. Takabatake, F. Teshima, H. Fujii, S. Nishigori, T. Suzuki, T. Fujita, Y. Yamaguchi, J. Sakurai, and D. Jaccard, *Phys. Rev. B* **41**, 9607 (1990).

- ¹²Y. Muro, K. Yamane, M.-S. Kim, T. Takabatake, C. Godart, and P. Rogl, *J. Phys. Soc. Jpn.* **72**, 1745 (2003).
- ¹³J. Kitagawa, T. Takabatake, E. Matsuoka, F. Takahashi, K. Abe, and M. Ishikawa, *J. Phys. Soc. Jpn.* **71**, 1630 (2002).
- ¹⁴P. Bonville, C. Godart, E. Alleno, F. Takahashi, E. Matsuoka, and M. Ishikawa, *J. Phys.: Condens. Matter* **15**, L263 (2003).
- ¹⁵R. Gumeniuk, W. Schnelle, H. Rosner, M. Nicklas, A. Leithe-Jasper, and Y. Grin, *Phys. Rev. Lett.* **100**, 017002 (2008).
- ¹⁶E. Bauer, A. Grytsiv, X.-Q. Chen, N. Melnychenko-Koblyuk, G. Hilscher, H. Kaldarar, H. Michor, E. Royanian, G. Giester, and M. Rotter *et al.*, *Phys. Rev. Lett.* **99**, 217001 (2007).
- ¹⁷D. Kaczorowski and V. H. Tran, *Phys. Rev. B* **77**, 180504 (2008).
- ¹⁸E. Bauer, X.-Q. Chen, P. Rogl, G. Hilscher, H. Michor, E. Royanian, R. Podloucky, G. Giester, O. Sologub, and A. P. Gonçalves, *Phys. Rev. B* **78**, 064516 (2008).
- ¹⁹R. Gumeniuk, K. O. Kvashnina, W. Schnelle, M. Nicklas, H. Borrmann, H. Rosner, Y. Skourski, A. A. Tsirlin, A. Leithe-Jasper, and Y. Grin, *J. Phys.: Condens. Matter* **23**, 465601 (2011).
- ²⁰M. Baenitz, R. Sarkar, R. Gumeniuk, A. Leithe-Jasper, W. Schnelle, H. Rosner, U. Burkhardt, M. Schmidt, U. Schwarz, D. Kaczorowski *et al.*, *Phys. Status Solidi B* **247**, 740 (2010).
- ²¹R. Gumeniuk, M. Schöneich, A. Leithe-Jasper, W. Schnelle, M. Nicklas, H. Rosner, A. Ormeci, U. Burkhardt, M. Schmidt, U. Schwarz *et al.*, *New J. Phys.* **12**, 103035 (2010).
- ²²R. Gumeniuk, L. Akselrud, K. O. Kvashnina, W. Schnelle, A. A. Tsirlin, C. Curfs, H. Rosner, M. Schöneich, U. Burkhardt, U. Schwarz *et al.*, *Dalton Trans.* **41**, 6299 (2012).
- ²³M. Nicklas, R. Gumeniuk, W. Schnelle, H. Rosner, A. Leithe-Jasper, F. Steglich, and Y. Grin, *J. Phys.: Conf. Series* **273**, 012118 (2011).
- ²⁴V. K. Pecharsky, L. L. Miller, K. A. Gschneidner, and D. C. Johnston, *Phys. Rev. B* **51**, 954 (1995).
- ²⁵S. Kirit, A. Thamizhavel, T. Takeuchi, K. Tabata, T. C. Kobayashi, A. Galatanu, E. Yamamoto, R. Settai, S. Ramakrishnan, and Y. Ōnuki, *J. Phys. Soc. Jpn.* **72**, 2338 (2003).
- ²⁶F. Ohtsu, H. Fukuoka, and S. Yamanaka, *J. Alloys Compd.* **487**, 712 (2009).
- ²⁷B. Penc, M. Hofmann, A. Szytuła, and A. Zygmunt, *J. Phys.: Condens. Matter* **13**, 4471 (2001).
- ²⁸G. Papanthanasios, P. Kotsanidis, J. Yakinthos, and W. Schaefer, *J. Alloys Compd.* **343**, 26 (2002).
- ²⁹Ł. Gondek, M. Guillot, A. Szytuła, M. Gutowska, and J. Więckowski, *Solid State Commun.* **147**, 313 (2008).
- ³⁰A. Gil, B. Penc, M. Hofmann, A. Szytuła, and A. Zygmunt, *J. Alloys Compd.* **322**, 21 (2001).
- ³¹O. Borisenko, O. Bodak, and Y. Seropegin, *Moscow Univ. Chem. Bull. (Engl. Transl.)* **49**, 103 (1994).
- ³²Y. Seropegin, O. Shepelyuk, J. Kurenbaeva, A. Gribanov, and O. Bodak, *J. Alloys Compd.* **299**, 241 (2000).
- ³³STOE Powder Software, WinXPow (version 2), Darmstadt, STOE and Cie GmbH, 2001.
- ³⁴L. Akselrud, P. Zavali, Y. Grin, V. Pecharsky, B. Baumgartner, and E. Wölfel, *Mater. Sci. Forum* **335**, 133 (1993).
- ³⁵W. Kabsch, *J. Appl. Cryst.* **26**, 795 (1993).
- ³⁶C. Paulmann, marToolsCP, Version 1.0, University of Hamburg, c/o HASYLAB/DESY, Germany (1993).
- ³⁷S. K. J. Johnas, W. Morgenroth, and E. Weckert, *HASYLAB/DESY Annual Report*, p. 325328 (2006).
- ³⁸L. J. Farrugia, *J. Appl. Cryst.* **32**, 837 (1999).
- ³⁹L. Akselrud and Y. Grin, xASWin program, Max-Planck-Institut für Chemische Physik fester Stoffe, Dresden, 2004.
- ⁴⁰R. Sarkar, R. Gumeniuk, A. Günther, A. Leithe-Jasper, W. Schnelle, Y. Grin, C. Geibel, and M. Baenitz (unpublished).
- ⁴¹L. Vasylichko, U. Burkhardt, W. Schnelle, H. Borrmann, F. Haarmann, A. Senyshyn, D. Trots, K. Hiebl, and Y. Grin, *Solid State Sci.* **14**, 746 (2012).
- ⁴²R. Gumeniuk, H. Borrmann, A. Ormeci, H. Rosner, W. Schnelle, M. Nicklas, Y. Grin, and A. Leithe-Jasper, *Z. Kristallogr.* **225**, 531 (2010).
- ⁴³K. Andres and E. Alberti, *Z. Metallk.* **27**, 126 (1935).
- ⁴⁴O. Bodak and E. Gladyshevskii, *Sov. Phys. Crystallogr.* **14**, 859 (1970).
- ⁴⁵B. Chabot, H. F. Braun, K. Yvon, and E. Parthé, *Acta Cryst. B* **37**, 668 (1981).
- ⁴⁶M. François, G. Venturini, E. McRae, B. Malaman, and B. Roques, *J. Less Common Metals* **128**, 249 (1987).
- ⁴⁷J. R. Salvador, J. R. Gour, D. Bilc, S. D. Mahanti, and M. G. Kanatzidis, *Inorg. Chem.* **43**, 1403 (2004).
- ⁴⁸J. Emsley, *The Elements* (Clarendon Press, Oxford, 1998).
- ⁴⁹V. Prabhawalkar and B. Padalia, *Curr. Sci.* **52**, 799 (1983).
- ⁵⁰J. M. Lawrence, G. H. Kwei, P. C. Canfield, J. G. DeWitt, and A. C. Lawson, *Phys. Rev. B* **49**, 1627 (1994).
- ⁵¹T. Hatwar, R. Nayak, B. Padalia, M. Ghatikar, E. Sampathkumaran, L. Gupta, and R. Vijayaraghavan, *Solid State Commun.* **34**, 617 (1980).
- ⁵²I. Felner, I. Nowik, D. Vaknin, U. Potzel, J. Moser, G. M. Kalvius, G. Wortmann, G. Schmiester, G. Hilscher, E. Gratz *et al.*, *Phys. Rev. B* **35**, 6956 (1987).
- ⁵³K. H. J. Buschow, U. Goebel, and E. Dormann, *Phys. Status Solidi B* **93**, 607 (1979).
- ⁵⁴B. C. Sales and D. K. Wohlleben, *Phys. Rev. Lett.* **35**, 1240 (1975).
- ⁵⁵W. Franz, F. Steglich, W. Zell, D. Wohlleben, and F. Pobell, *Phys. Rev. Lett.* **45**, 64 (1980).
- ⁵⁶A. Kowalczyk, M. Falkowski, and T. Toliński, *J. Appl. Phys.* **107**, 123917 (2010).
- ⁵⁷V. T. Rajan, *Phys. Rev. Lett.* **51**, 308 (1983).
- ⁵⁸F. Iga, S. Hiura, J. Klijn, N. Shimizu, T. Takabatake, M. Ito, Y. Matsumoto, F. Masaki, T. Suzuki, and T. Fujita, *Physica B* **259–261**, 312 (1999).
- ⁵⁹R. Troć, *J. Alloys Compd.* **442**, 34 (2007).
- ⁶⁰K. Kadowaki and S. Woods, *Solid State Commun.* **58**, 507 (1986).
- ⁶¹N. Tsujii, K. Yoshimura, and K. Kosuge, *JPCM* **15**, 1993 (2003).
- ⁶²L. B. Farhat, M. Amami, E. Hlil, and R. B. Hassen, *J. Alloys Compd.* **485**, 701 (2009).
- ⁶³K. Alami-Yadri, D. Jaccard, and D. Andreica, *J. Low Temp. Phys.* **114**, 135 (1999).
- ⁶⁴U. Gottwick, K. Gloss, S. Horn, F. Steglich, and N. Grewe, *J. Magn. Magn. Mater.* **47–48**, 536 (1985).
- ⁶⁵F. Iga, T. Suemitsu, S. Hiura, K. Takagi, K. Umeo, M. Sera, and T. Takabatake, *J. Magn. Magn. Mater.* **226–230**, 137 (2001).
- ⁶⁶T. Saso and K. Urasaki, *J. Phys. Soc. Jpn.* **71S**, 288 (2002).
- ⁶⁷F. Pobell, *Matter and Methods at Low Temperatures* (Springer, Berlin, 1996).
- ⁶⁸H. Schneider and D. Wohlleben, *Z. Phys. B* **44**, 193 (1981).
- ⁶⁹F. G. Aliiev, R. Villar, S. Vieira, M. A. Lopez de la Torre, R. V. Scolozdra, and M. B. Maple, *Phys. Rev. B* **47**, 769 (1993).

- ⁷⁰M. B. Hunt, M. A. Chernikov, E. Felder, H. R. Ott, Z. Fisk, and P. Canfield, *Phys. Rev. B* **50**, 14933 (1994).
- ⁷¹A. P. Reyes, R. H. Heffner, P. C. Canfield, J. D. Thompson, and Z. Fisk, *Phys. Rev. B* **49**, 16321 (1994).
- ⁷²T. Shimizu, M. Takigawa, H. Yasuoka, and J. Wernick, *J. Magn. Magn. Mater.* **52**, 187 (1985).
- ⁷³H. Okamura, T. Michizawa, T. Nanba, and T. Ebihara, *J. Phys. Soc. Jpn.* **73**, 2045 (2004).
- ⁷⁴J. Klaasse, F. de Boer, and P. de Châtel, *Physica B* **106**, 178 (1981).