Unusual weak magnetic exchange in two different structure types: YbPt$_2$Sn and YbPt$_2$In

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Received 5 August 2014, revised 12 September 2014
Accepted for publication 19 September 2014
Published 17 October 2014

Abstract

We present the structural, magnetic, thermodynamic and transport properties of the two new compounds YbPt$_2$Sn and YbPt$_2$In. X-ray powder diffraction shows that they crystallize in different structure types, the hexagonal ZrPt$_2$Al and the cubic Heusler type, respectively. Despite quite different lattice types, both compounds present very similar magnetic properties: a stable trivalent Yb$^{3+}$, no evidence for a sizeable Kondo interaction and very weak exchange interactions with a strength below 1 K as deduced from specific heat $C(T)$. Broad anomalies in $C(T)$ suggest short range magnetic ordering at about 250 mK and 180 mK for YbPt$_2$Sn and YbPt$_2$In, respectively. The weak exchange and the low ordering temperature result in a large magnetocaloric effect as deduced from the magnetic field dependence of $C(T)$, making these compounds interesting candidates for magnetic cooling. In addition we found in YbPt$_2$In evidences for a charge density wave transition at about 290 K. The occurrence of such transitions within several RET$_2$X compound series (RE = rare earth, T = noble metal, X = In, Sn) is analyzed.

Keywords: rare earth compounds, magnetism, charge density wave, magnetic cooling, structure

(Some figures may appear in colour only in the online journal)

1. Introduction

In the last decade Yb-based intermetallic compounds have attracted considerable attention because of the observation of unconventional and unique properties in quite a number of cases. Prominent examples are: (i) the heavy fermion compound YbRh$_2$Si$_2$, which is one of the most interesting system for studying quantum critical points [1,2]; (ii) YbAlB$_4$, the only Yb-based unconventional superconductor, where superconductivity seems to emerge from valence fluctuations instead of the commonly assumed antiferromagnetic fluctuations [3,4] and (iii) the series YbT$_2$Zn$_{20}$, which present the highest mass renormalization observed up to now in strongly correlated electron systems [5,6]. These unusual properties emerge from the instability of the 4$f$ shell of Yb and the associated valence instability of this element. In the divalent Yb$^{2+}$ state the 4$f$ shell is fully occupied and therefore non-magnetic. In the trivalent Yb$^{3+}$ state one hole in the 4$f$ shell yield a local 4$f$ moment with $S = 1/2$, $L = 3$ and thus $J = 7/2$ according to Hund’s rules. However, in quite a number of Yb-based compounds a strong hybridization between the 4$f$ and the conduction electrons results in an intermediate valent state or in the formation of a Kondo lattice. In such systems the interaction of the 4$f$ electrons with the conduction electrons results in strong electronic correlation effects and a huge renormalization of the quasi particles at the Fermi level, hence the name heavy fermion.
The discovery of these interesting phenomena motivates the search for new Yb-based intermetallic compounds with unusual properties. In the present paper we report the synthesis of the new compounds YbPt2Sn and YbPt2In as well as the investigation of their structural and magnetic properties. While the related system YbPd2Sn has been widely investigated quite some time ago and was found to show coexistence of classical superconductivity below $T_c = 2.3$ K and antiferromagnetism of localized trivalent Yb below $T_N = 0.22$ K [7, 8], neither YbPt2Sn nor YbPt2In have yet been reported. Our results revealed these two compounds to crystallize in very different structure types. Nevertheless, they exhibit similar magnetic properties: in both compounds Yb is in a stable trivalent state, without any evidence for the strong correlation effects searched for. In contrast, the exchange interactions are exceptionally weak, resulting in a quite large calculated magnetocaloric effect. Thus instead of being of interest for the field of strongly correlated electron systems, both compounds turned out to be promising candidates for magnetic cooling. Furthermore, in YbPt2In we observe at about 290 K evidence for a structural phase transition, likely of charge density wave (CDW) type. Similar structural phase transitions have already been reported in several RET2X compound series (RE=rare earth, T=noble metal, X=In, Sn) crystalizing in the cubic Heusler structure type. A comparative analysis of these series of compounds reveals a systematic trend: the occurrence of this phase transition seems to be connected with the change from the hexagonal ZrPt2Al to the cubic Heusler structure type within a compound series. This change is governed by the size of the RE atom and by the main quantum number of the noble metal, while the total number of valence electrons does not seem to be important.

2. Sample preparation

The REPt2Sn and REPt2In series of compounds were first reported in 1987 by A E Dwight for RE=Gd, Tb, Er, Tm and Gd–Ho, respectively [9]. All samples were found to crystallize in the hexagonal ZrPt2Al structure type. For the Gd-based compounds this was later confirmed by K Zhang and L. Chen [10] as well as by B Heying et al [11]. However, we did not find any report on the Yb- or on the Lu-based homologues. Because of the huge difference in the melting points of the pure elements ($T_{Pt} \approx 2040$ K, $T_{Yb} \approx 1100$ K, $T_{Sn} \approx 500$ K and $T_{In} \approx 430$ K) we prepared the polycrystalline samples in a two-stage arc-melting process under ultrapure argon atmosphere. In a first stage an appropriate amount of Yb and of the low melting elements Sn or In was melted to a small button. In the second step Pt was added and melted with the preracted YbSn/YbIn mixture. In this step the samples were repeatedly melted and turned over to enhance homogeneity. For both compounds the total weight loss after the whole procedure was about 4 wt%. This can safely be attributed to the evaporation of Yb due to its low boiling point of 1469 K. Therefore, the sample were investigated in the as-cast state. Since preliminary results indicated a lower phase purity in the as-cast YbPt2In ingots, they were put into a Tungsten boat, wrapped with Tantalum foil and annealed at 1073 K for 100 h under 800 mbar purified argon. Microprobe analysis revealed that the annealed YbPt2In samples still include some unreacted Pt and small amounts of Yb-deficient phases. The precise control of the Yb content during the preparation of these compounds is likely the main problem in enhancing the sample quality. The homologue non-magnetic counterparts LuPt2Sn and LuPt2In have been synthesized by the same procedure.

3. Experimental details

Room temperature x-ray powder diffraction data were recorded on a STOE Stadip instrument in transmission mode and using Cu $K\alpha1$ radiation. X-ray powder spectra of freshly crushed YbPt2In showed broadened Bragg peaks (shown in figure 1(b)). Annealing the powder again resulted in a significant narrowing of the peaks, but at the same time the size and number of foreign phase peaks increase, likely due to surface oxidation (not shown). The lattice parameters refinement by least-squares fitting as well as Rietveld refinements have been done using the program package Wincsd [12]. The low-temperature diffraction experiments were carried out using a Siemens D500 powder diffractometer, equipped with a closed cycle helium refrigerator. The accessible sample temperature range extends from 10 K to 300 K. The samples were placed directly on a temperature controlled Cu block by means of Apiezon N grease to ensure good thermal contact. For temperature control a silicon diode temperature sensor was used that was mounted inside this Cu block directly beneath the sample. At each temperature the powdered sample was carefully thermalized before starting the diffraction scan. The diffraction scans were recorded with Cu $K\alpha1$ radiation. The resistivity $\rho(T)$ and specific heat capacity $C(T)$ were measured in the $T$ range of 350 mK–400 K using a commercial Quantum Design (QD) PPMS equipped with a $^3$He option. $C(T)$ in the millikelvin range down to around 50 mK was determined in a $^3$He/$^4$He dilution refrigerator using a compensated heat pulse method. The magnetization and susceptibility measurements above 1.8 K were carried out using a QD SQUID VSM, while low-temperature $M(H)$ and $\chi(T)$ data were taken using a QD MPMS equipped with a $^3$He option.

4. Experimental results and discussion

4.1. Structure at room temperature

Surprisingly, an examination of the x-ray powder diffraction patterns of YbPt2Sn and YbPt2In shows that they crystallize in completely different structure types (figure 1). In YbPt2Sn all peaks, except for two very weak ones ($2\theta \approx 42^\circ$ and $44^\circ$) could be assigned to the hexagonal ZrPt2Al structure type, space group $P6_3/mmc$, with the lattice parameters $a = 4.4862(5)$ Å and $c = 8.8881(8)$ Å. This structural model was then used for a Rietveld refinement of the powder
Figure 1. Powder x-ray diffraction patterns of YbPt$_2$Sn and YbPt$_2$In at room temperature. The grey bars at the bottom of the diagrams indicate the location of Bragg peaks of the hexagonal ZrPt$_2$Al and of the cubic Heusler phase structure types, respectively. The pictures of the structures illustrate the quasi-2D character with alternating Yb and Pt$_2$Sn layers for YbPt$_2$Sn, contrasting the 3D-network in cubic YbPt$_2$In. (a) For YbPt$_2$Sn all reflexes except for two faint lines were indexed, the indices are only given for the strongest peaks. The bottom part shows the difference between $I_{\text{obs}}$ and $I_{\text{calc}}$ (see text). (b) In YbPt$_2$In the pattern is dominated by the strong peaks corresponding to the a/2 bcc underlying structure, but the (1 1 1) and (2 0 0) peaks corresponding to the ordering of Yb, Pt and In in the Heusler phase are well observed. The origin of the additional peaks is discussed in the text.

Table 1. Crystallographic data for YbPt$_2$Sn at room temperature (structure type ZrPt$_2$Al, space group $P6_3/mmc$, $Z = 2$).

| Parameter     | Value         |
|---------------|---------------|
| $a$ (Å)       | 4.4862(5)     |
| $c$ (Å)       | 8.8881(8)     |
| $V$ (Å$^3$)   | 154.92(4)     |
| $\rho$ (g cm$^{-3}$) | 14.6(1) |
| $\theta_{\text{max}}$ (deg) | 90       |
| Reference parameters | 8          |
| $R_{\text{int}}$; $R_p$ | 0.0568; 0.110 |

The refinement confirmed the ZrPt$_2$Al type of structure as evidenced by the small difference (curve in bottom of figure 1(a)) between observed ($I_{\text{obs}}$, open circles in figure 1(a)) and calculated ($I_{\text{calc}}$, continuous lined) diffraction pattern. Reasonable reliability factors and displacement parameters were obtained for the fully ordered structure, excluding the presence of strong disorder. The structural parameter obtained within this refinement are given in table 1. All indexed peaks are marked with grey bars and the strongest ones labeled with the corresponding indices. The small number and weak intensities of unidentified peaks confirms an almost phase pure sample as already deduced from microprobe investigations. The same result was also observed for LuPt$_2$Sn, with only slightly smaller lattice parameters $a = 4.4803(5)$ Å and $c = 8.8765(9)$ Å. Comparing volume per formula unit within the REPt$_2$Sn compound series using in addition the data of [9] reveals a continuous decrease with increasing atomic number of the rare earth: $V_{\text{Er}} = 78.30$ Å$^3$, $V_{\text{Tm}} = 77.94$ Å$^3$, $V_{\text{Yb}} = 77.46$ Å$^3$ and $V_{\text{Lu}} = 77.15$ Å$^3$. This indicates Yb to be in the trivalent state. The picture of the YbPt$_2$Sn structure shown in figure 1(a) evidences some quasi-2D character with an alternation of Yb and Pt$_2$Sn layers.

In contrast, the few strong Bragg reflections in the x-ray pattern of YbPt$_2$In (figure 1(b)) initially indicate a simple body-centered cubic (bcc) underlying structure. However, ordering of Yb, Pt and In in a cubic Heusler structure type ($L2_1$, $Fm\overline{3}m$) is clearly evidenced by the appearance of the (1 1 1) and (2 0 0) peaks. The x-ray pattern of YbPt$_2$In is less clean than that of YbPt$_2$Sn, in accordance with the larger amount of foreign phases observed with microprobe. However, as discussed later, some of the weak peaks initially suspected to belong to foreign phases turned out to be intrinsic superstructure peaks connected with the formation of a CDW. Because of the formation of the CDW phase, a refinement of the 300 K diffraction pattern using the cubic Heusler structure is not meaningful, while the low $T$ structure cannot be determined.
because in the powder pattern the sparse superstructure peaks are too weak. A similar result was also observed for LuPt2In.

The main difference is a slight decrease of the lattice parameter from \(a = 6.655(3) \text{ Å}\) for the Yb-based to \(a = 6.6484(7) \text{ Å}\) for the Lu-based compound. Thus, our results evidence that within the REPt2In series of compounds the structure changes for the Lu-based compound. Thus, the volume per formula unit of HoPt2In, \(V_{\text{Ho}} = 79.10 \text{ Å}^3\), is significantly larger than that of YbPt2In and LuPt2In, \(V_{\text{Yb}} = 73.68 \text{ Å}^3\) and \(V_{\text{Lu}} = 73.47 \text{ Å}^3\), respectively. The difference being much larger than expected from the lanthanide contraction. This indicates that the Heusler structure type is denser than the hexagonal one. On the other hand, the volume difference between YbPt2In and LuPt2In is smaller than that for the Sn homologs. This indicates Yb to be in the trivalent state in YbPt2In, too. The 3D network of cubic YbPt2In is shown in figure 1(b).

4.2. Weak exchange interactions

The temperature dependence of the inverse susceptibility \(\chi^{-1}(T)\) of YbPt2Sn in an external field of \(\mu_0 H = 0.1 \text{ T}\) is shown in inset (a) of figure 2. It displays an almost linear behavior, which can be nicely fitted above 100 K to a Curie–Weiss \((\chi^{-1} = (T + \Theta)/C_{\text{CW}})\) law with an effective moment \(\mu_{\text{eff}}^{\text{high}} = 4.52 \mu_B\) very close to the value for the stable trivalent Yb\(^{3+}\) state \(4.53 \mu_B\). In Yb-based systems the Weiss temperature \((\Theta_{\text{high}} = -15 \text{ K})\) obtained from the fit at high temperatures is usually determined by crystal electric field (CEF) effects since exchange is typically very weak due to the small de Gennes factor. A more reliable estimation of exchange strength can be obtained from a Curie–Weiss fit of \(\chi^{-1}\) in the low temperature range (shown in the central part of figure 2). The fitted low \(T\) Weiss temperature \(\Theta_{\text{low}} = -0.08 \text{ K}\) is a first indicator of weak Yb–Yb intersite exchange. The negative sign suggest a dominant ferromagnetic (FM) interaction, but considering the very small value and the large range of the extrapolation, this conclusion is not very reliable. Towards lowest temperatures \(\chi^{-1}\) shows the beginning of an upturn, but this might be the result of the onset of saturation due to magnetic energy becoming comparable to thermal energy. This is confirmed by the field dependence of the magnetization at \(T = 0.5 \text{ K}\) shown in figure 2(b). The experimental data, which show a well-defined saturation above 0.5 T to a value slightly larger than \(2 \mu_B\), are compared with an effective \(S = 1/2\) Brillouin function for \(T = 0.5 \text{ K}\) with the only free parameter, the saturation magnetization, fixed to \(M_{\text{sat}} = 2.3 \mu_B/\text{Yb}\). The nice agreement with this single ion model confirms the weakness of the exchange interactions. The saturation moment is of the size typically expected for the doublets resulting from the splitting of the \(J = 7/2\) multiplet of Yb\(^{3+}\) induced by the CEF.

The susceptibility and magnetization data of YbPt2In are almost identical to those of YbPt2Sn (figure 3). The only noticeable difference is a positive Weiss temperature, with a low \(T\) value \(\Theta_{\text{low}} = 0.31 \text{ K}\) indicating weak, but dominantly antiferromagnetic (AFM) exchange. Since the similarity is clearly visible in the data above 1.75 K and is supported by specific heat data down to lowest temperatures and because of limited measuring time in the \(^3\text{He}\) equipment, susceptibility and magnetization were not investigated below 1.75 K.

While the tiny Weiss temperatures point to the weakness of the exchange between \(4f\) moments, the small values might also be the result of competing FM and AFM interactions.
Figure 3. Temperature dependence of $\chi^{-1}$ of YbPt$_2$In in a magnetic field of 0.1 T. Analysis similar to that for YbPt$_2$Sn in figure 2 yield $\mu_{\text{eff}}^{\text{high} T} = 4.44 \mu_B$, $\mu_{\text{eff}}^{\text{low} T} = 3.52 \mu_B$ and $\Theta_{\text{low} T} = 0.31$ K. Inset (b) shows the magnetization measured as a function of field at $T = 1.75$ K.

Figure 4. (a) Temperature dependence of the measured specific heat of YbPt$_2$Sn and YbPt$_2$In in fields of 0 T and 4 T. At $\mu_0 H = 0$ T the strong increase below 2 K and peaks near 240 mK and 180 mK for the Sn and the In compound, respectively, indicate magnetic order of local moments dominated by short range correlations. A magnetic field of 4 T results in a Schottky anomaly at around 3 K because of the Zeeman splitting of the 4$f$ states. The increase at low $T$ is due to the nuclear Yb contribution. (b) Temperature dependence of the entropy deduced from $C(T)$ data after subtraction of a nuclear and a phonon contribution. Above 1 K $S^{4f}(T)$ levels out at nearly $R \ln 2$ indicating a well separated crystal field ground state doublet for both systems. In both compounds $1/2 R \ln 2$ is reached at $T = 0.4$ K, indicating the overall strength of the exchange to be below 1 K.

This can be discriminated by studying the magnetic specific heat. Within a Heisenberg model for local moment systems, the leading term in the high temperature series expansion for the specific heat is proportional to the sum of the square of all exchange interactions. Therefore, AFM and FM terms do not cancel out as for the Weiss temperature, instead they are additive. Thus the specific heat at higher temperatures and the $T$ dependence of the entropy are more appropriate for the determination of the overall strength of exchange interactions. We have measured the specific heat $C(T)$ of both compounds down to 60 mK. Figure 4(a) shows a log($C/T$) versus log$T$ plot of the measured data in the temperature range between 60 mK and 4 K and in a magnetic field of 0 T and 4 T. The results are quite similar for both compounds: in zero field $C/T$ shows a clear minimum at around 3.3 K (YbPt$_2$Sn) or 2.5 K (YbPt$_2$In) from which on it increases continuously with decreasing $T$, following roughly a power law $C/T \propto T^{-2}$ over one decade in temperature. This increase ends in a broaden anomaly at $T_0 = 250$ mK and $T_0 = 180$ mK for YbPt$_2$Sn and YbPt$_2$In, respectively. With further decreasing temperature $C/T$ stays...
Accordingly, the broad anomalies at \( T_0 \) have to be attributed to the emergence of intersite correlations. (in three different magnetic Yb species statistically distributed on the single crystallographic Yb site. Our calculations indicate that the overall splitting due to hyperfine coupling can be of the order of 300 mK for Yb\( ^{171} \) and 500 mK for Yb\( ^{173} \), thus larger than the observed \( T_0 \).

In order to gain more insight into the strength of exchange interactions, we determined the \( T \) dependence of the entropy \( S^{\alpha} / T \) for both compounds. For this purpose the nuclear contribution was estimated from the experimental data in 4 T (see above) while the phononic contribution was estimated from the homologue Lu-compounds. Both were subtracted from the data and then \( S^{\alpha} / T \) was calculated by integrating \( C(T)/T \). We first note that in zero field \( S^{\alpha} \) saturates above 1 K at a value of about 5.1 K\(^{-1}\) mol\(^{-1}\), thus close to the \( T_0 \) expected for a doublet. This confirms our interpretation of the \( C(T)/T \) data and indicates that our estimates of the nuclear parts are reasonable. A first estimation of the strength of exchange interactions can be obtained by taking twice the temperature at which \( S^{\alpha} \) reaches 1/2 \( T_0 \), which gives an overall scale of about 0.8 K for both compounds. This value is significantly larger than expected from the Weiss temperatures. As noted above, this discrepancy suggests competition between FM and AFM exchange. An idea about the strength of competing interaction can be obtained from a slightly more involved analysis assuming a Heisenberg model with exchange between nearest neighbors (NN) and next nearest neighbors (NNN). For such a model, the leading term in the 1/\( T \) series expansion of the specific heat is given by

\[
C = \frac{\mu^2 H}{3} \cdot \frac{1}{T^2} \cdot \sum_i J_i = \frac{\mu^2 H}{4} \cdot \frac{1}{T^2},
\]

where the Weiss temperature is given by \( \Theta_0 = 1/4 \cdot \sum J_i \), where \( J_i \) is the exchange strength (in Kelvin) to the neighbor \( i \). From the evolution of \( C(T)/T \) in the temperature range \( 1 \, K < T < 2 \, K \) one can estimate \( \alpha \) to be of the order of 1.2 KJ mol\(^{-1}\) in both compounds. In the hexagonal structure of YbPt\(_2\)Sn the Yb atom has 6 NN within the hexagonal plane and 6 NNN in the planes above and below. In this compound the negative sign of \( \Theta_0 \) implies one of the exchange to be negative, i.e. ferromagnetic and the other to be positive, i.e. antiferromagnetic. Using the expressions given above, one can easily deduce from the values of \( \alpha \) and \( \Theta_0 \) the magnitude of these exchanges: we obtained \( J_{AFM} = -0.33 \, K \) and \( J_{FM} = 0.27 \, K \). In the cubic Heusler structure, is disorder due to partial substitution of Pt by Sn/In and vice versa. Notably strong fluctuations far above a broad magnetic transition at comparatively low temperatures

5 Using standard mathematical operation, we got the following relation between the strength of the exchange interactions, the coefficient \( \alpha \) of the \( T^{-2} \) term in \( C(T) \) and \( \Theta \). We first define the quantities \( A = 32\alpha /18\pi R \) (\( R \) = gas constant) and \( B = 2\alpha/3 \). Then for YbPt\(_2\)Sn and Yb\( ^{169}\)Pt\(_2\)Sn we obtained \( J_{AFM} = (B + C)/2 \) and \( J_{FM} = (B - C)/2 \) while for Yb\( ^{167}\)Pt\(_2\)Sn with 12 NN \( (J_1) \) and 6 NNN \( (J_2) \) there are two solutions, one with \( J_1 = (B + C)/3 \) and \( J_2 = (B - C)/3 \) and one with \( J_1 = (B - C)/3 \) and \( J_2 = (B + C)/3 \), where \( C = \sqrt{3}/2 - B^2/2 \).
Figure 5. Temperature dependence of the resistivity $\rho$ of YbPt$_2$Sn and YbPt$_2$In. The positive slope proves a metallic character in both compounds. The anomaly at about 190 K (decreasing $T$) and 290 K (increasing $T$) in YbPt$_2$In evidences a first order phase transition, probably of charge density wave type (see text). The large residual resistivity likely indicates the presence of some atomic disorder in both compounds.

structure$^6$ of YbPt$_2$In the Yb atom has 12 NN and 6 NNN, and we define the respective exchanges as $J_1$ and $J_2$. Because the number of NN and NNN differs, we obtain two solutions from $\alpha = 1.2$ K mol$^{-1}$ and $\Theta = 0.31$ K: $J_1 = 0.27$ K and $J_2 = -0.33$ K, or $J_1 = -0.13$ K and $J_2 = 0.47$ K.$^7$

All these results point to unusual weak exchange interactions for a dense intermetallic magnetic rare earth compound. One criterion is obviously the small de Gennes factor of Yb, which is e.g. a factor of 50 smaller than that of Gd. For heavy rare earth ($\geq$Gd) magnetic ordering temperatures roughly scale with the de Gennes factor resulting in comparatively small ordering temperatures in Yb compounds. But even within Yb based intermetallic systems, the strength of the exchanges observed here are very weak. The origin for this weak exchange is still an open question. It is unlikely to be related to specific structural properties, since we observed a similar effect in two completely different structure types. Likely it is more related to the combination of a heavy 5d and a heavy 5p ligands. This very tiny exchange opens a way for a possible application: part (b) of figure 4 shows a huge shift of the entropy upon applying a comparatively small field of 4 T. This indicates a huge magnetocaloric effect and suggest these materials to be interesting candidates for adiabatic cooling.

4.3. Structural transition

The temperature dependence of the resistivity $\rho(T)$ shown in figure 5 reveals a continuous increase from lowest to highest temperatures, without strong changes in the slope, except for an anomaly in YbPt$_2$In at around 240 K upon heating and 170 K upon cooling. The general behavior of $\rho(T)$ indicates a standard metallic character and the absence of Kondo interaction. On the other hand the anomaly observed in YbPt$_2$In and its large hysteresis suggests the presence of a first order phase transition. This anomaly was reproduced in different samples, although the transition temperature $T_{\text{trans}}$ (midpoint) varies from sample to sample from about 240 K to more than 400 K. We suspect this sample dependence to be related to slightly different Yb contents since its control is difficult in the arc-melting process. In figure 5 we show the result for the sample with the sharpest kink. Furthermore, its $T_{\text{trans}}$ was below 300 K and thus easily accessible. The upturn in $\rho(T)$ at $T_{\text{trans}}$ points to the opening of a gap on part of the Fermi surface and is reminiscent of spin or charge density wave (SDW or CDW) transitions. Since a SDW transition at around 250 K is very unlikely in view of the weakness of magnetic interactions, this anomaly is an indication for the occurrence of a CDW in YbPt$_2$In.

Therefore, we performed $T$ dependent powder x-ray scattering in order to obtain direct evidence for a structural transition. For these measurements part of the sample used for the $\rho(T)$ curve shown in figure 5 was powdered to a particle size of less than 20 $\mu$m. The diffraction patterns did not reveal any significant splitting of the main peaks of the Heusler phase, but the appearance of several weak additional superstructure peaks below 300 K. This is demonstrated in figure 6 which shows the strong (2 2 0) peak of the Heusler structure and one of the strongest additional peak (superstructure peak) which emerges at a smaller scattering angle for $T < 300$ K. The evolution of the intensity of both the additional and the main peak reveal a hysteresis as was observed in $\rho(T)$. The appearance of additional peaks at a similar temperature as the anomaly in $\rho(T)$ and with a similar hysteresis confirms the presence of a structural phase transition in YbPt$_2$In.

For a more precise analysis the diffraction patterns shown in figure 6 and additional ones at further temperatures were fitted with a sum of three Lorentzians: one with all parameter free for the strong (2 2 0) peak, one with a fixed line width for the additional low angle superstructure peak and a third one with all parameter fixed in order to account for a suspected small satellite peak near 37.95 deg. The position of the (2 2 0) peak shifts continuously to higher angle with decreasing $T$, but analysis of the whole diffraction pattern proves that this shift is merely due to the normal lattice contraction upon cooling since all strong peaks shift correspondingly. Furthermore, we could not resolve any significant increase in the width of this peak, indicating that any splitting is very small. In contrast its intensity decreases significantly with $T$, in contradiction

$^6$ See footnote 5.

$^7$ See footnote 5.
Figure 6. Evolution of the (2 2 0) Bragg peak with increasing temperature in YbPt$_2$In. Above 200 K the weak superstructure peak at 37.55 deg starts to disappear proving a structural phase transition. The shift of the central (2 2 0) peak to lower angle is due to the normal thermal expansion. The data suggest a further satellite peak near 37.95 deg.

To the expected increase due to the increasing Debye Waller factor. Part of this intensity is transferred to the superstructure peak. The finite intensity of this peak at 300 K is likely related to the problem of determining the correct background, but might also be due to some part of the sample being still in the low T phase at 300 K. Interestingly, the position of this peak does not shift with T, implying that the effect due to the contraction of the lattice is compensated by a change in the structural deformation of the low T phase. The absence of a visible splitting of the main peaks and the appearance of several weak additional peaks indicate that the low T structure is mainly a modulation of the cubic high T structure resulting in a multifold extended cell, as was already suggested for UPd$_2$In [17]. This supports the CDW character of the transition. Because of the small number of superstructure peaks visible in the powder data and their weak intensity, the low T structure could not be determined. This requires studies on single crystals, which have now been started. Preliminary studies on LuPt$_2$In also indicate the occurrence of a CDW transition at about 480 K.

Low T structural transitions have already been reported in some RET$_2$X compounds with Heusler structure. Thus, in the series REAu$_2$In a transition has been found for RE = La–Nd, with $T_{trans}$ decreasing with increasing size of the RE atom [23]. Accordingly all members of this series with RE heavier than Nd stay in the cubic structure down to lowest T. Our present observations suggest a systematic trend for the occurrence of this transition. In order to disclose underlying relations we show in figure 7 the evolution of the structure across RET$_2$X series with either ZrPt$_2$Al or Heusler structure types [9, 18–24]. In horizontal direction the table is arranged according to decreasing size of RE, while in the vertical direction the series are arranged according to increasing stability of the cubic structure. This table evidences several trends: the transition from the hexagonal ZrPt$_2$Al to the Cubic Heusler structure type is promoted by:

- a decrease of the size of RE
- replacement of a 5d T metal by a 4d T metal
- replacement of a T metal from the Ni column by one of Cu column
- replacement of Sn by In

On the other hand, the total number of valence electrons seems to be irrelevant. The table suggests a further correlation: in the compounds with a cubic Heusler structure at high T, the structural transition at low T is only observed if the compound is close to the border to the hexagonal structure. Thus, the occurrence of the structural low T transition seems to be related to an incipient instability of the cubic Heusler structure towards a completely different structure type. However the low T structure seems to be quite different for the different series or even within a series. Thus, DyPd$_2$Sn and the REAu$_2$In (RE = La–Nd) present a strong and well-defined splitting of the cubic peaks indicating a cubic to tetragonal transition, while TbPd$_2$Sn and UPd$_2$In present a splitting in multiple peaks indicating a complex low T structure [17, 18, 23]. Unfortunately, the low T structure has yet not be determined in any of these compounds.

5. Conclusion

We have synthesized the two new compounds YbPt$_2$Sn and YbPt$_2$In and found that they crystallize in very different structure types, in the hexagonal ZrPt$_2$Al and in the cubic Heusler ones, respectively. Despite different structures the two compounds present very similar magnetic properties indicating a stable trivalent Yb$^{3+}$ experiencing rather weak exchange interactions with a strength well below 1 K. Specific heat data evidence short range ordering at about 200 mK, but with strong intersite fluctuations up to 2 K. The reduced stability of
the ordered state is likely due to both geometrical frustration and competing FM and AFM interactions, as indicated by a combined analysis of specific heat and susceptibility results. In Yb-based systems magnetic exchange is expected to be weak because of the small de Gennes factor, but in the present compounds the strength of magnetic interactions is particularly weak compared to other intermetallic Yb-based compounds. This might be related to the ligands being heavy 5d and heavy 5p elements. The weakness of the exchange interactions results in a large magnetocaloric effect, which make these compounds attractive candidates for magnetic cooling.

Furthermore, we discovered in YbPt2In a first order phase transition at about 290 K, to a yet undetermined low T structure which is likely a complex superstructure resulting from a multifold extended cell. At the transition we observe a clear increase in ρ(T) with decreasing T, indicating partial gapping of the Fermi surface. This suggests this transition to be a charge density wave. Similar transitions have previously been reported for a few RET2X compounds crystallizing in the cubic Heusler structure. By analyzing the evolution of the structure in several RET2X series of compounds we could relate the occurrence of this low T structural transition to the change of the high T structure from the hexagonal to the cubic one and disclose the parameters which govern this change in the high T structure.

Acknowledgments

This work was financially supported by the Max-Planck-POSTECH Center for complex Phase Materials KR2011-0031558 and by the German Research Foundation (DFG), grant GE602/2-1. The work in Frankfurt was supported through the SFB/TR49. Additional DFG support within the Research Training Group ‘Itinerant magnetism and superconductivity in intermetallic compounds’ (DFG-GRK1621) is acknowledged.

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