High Pressure Synthesis of a New Phase of YbAg₂: Structure, Valence of Yb and Properties

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Abstract

The new phase of YbAg₂ was obtained using high-pressure and high-temperature reaction. YbAg₂ crystallizes in the MgZn₂ structure (the space group $P6_3/mmc$ space group, № 194) with $a = 5.68153(3)$ Å and $c = 9.31995(7)$ Å and the unit cell volume $V = 260.54(3)$ Å³. The XANES analysis showed that the valence state of Yb is +2.8. The low-temperature dependences of the electrical resistivity and magnetic susceptibility can be adequately described by a T^2 term that supports the Fermi-liquid picture. The Kadowaki-Woods relation gives a low value of the degeneracy ($N = 2$).

1. Introduction

Over the past few years, a considerable number of studies have been conducted on the ytterbium compounds since they display a rich variety of intriguing physical phenomena such as Kondo and heavy fermion behavior, quantum criticality, non-Fermi liquid behavior and so on [1]. These properties are highly sensitive to the chemical environment as well as to external pressure, magnetic field or temperature. This is due to the fact that in the atomic state, Yb is divalent with a filled f^{14} shell, but in a solid, the f electrons may play an active role in the formation of the electronic band structure. For example, pressure reduces the unit cell volume, that leads to the trivalent magnetic Yb³⁺($4f^{13}$) state rather than to the divalent nonmagnetic Yb²⁺($4f^{14}$) state.

It is known that at ambient pressure the compound YbAg₂ in which ytterbium ion is divalent and non-magnetic crystallizes in the orthorhombic structure of the CeCu₂ type [2]. We performed the high-pressure and high-temperature reaction in the composition Yb:2Ag and have successfully obtained the new high pressure phase.

2. Experiment

Samples were prepared by melting of the constituent materials at a constant pressure of 5 GPa. Initial purities of Ag and Yb powders were 99.99% and 99.9%, respectively. Pellets of well-mixed powdered constituents were placed in rock-salt tubular ampoules with the end caps of silver and directly heated electrically up to $T \approx 1450$ °C (that is well above the melting temperature of NaCl at 5 GPa) [3]. Then samples were rapidly quenched to room temperature, and pressure was released.

The high pressure was generated in a pressure cell of the “toroid” type [4]. The resulting material was a uniform polycrystal.

Powder XRD pattern of the compound was collected on HUBER (G670) diffractometer with Cu K $_{\alpha 1}$ radiation in transmission mode, at 2 θ step 0.005° in the angular range from 4 to 95 degrees at room temperature. Crystal structure was investigated by Rietveld full-profile analysis of XRD pattern, using Fullprof [5] and WinPLOT [6] programs. Peak shapes were fitted by the Pseudo-Voigt function. Background was described by linear interpolation of background points.

The electrical resistivity measurements were performed on bulk polycrystalline samples using a lock-in detection technique (SR830 lock-in amplifier) in the temperature range of 2 ÷ 300 K. The specific heat and transport measurements for $T \geq 0.5$ K were performed in a Quantum Design PPMS system with a ^3He insert. Measurements of the magnetic susceptibility were performed for $T \geq 5$ K with Quantum Design MPMS SQUID magnetometer.

The X-ray absorption measurements using synchrotron radiation were carried out at I811 beamline of MAX IV facility (Lund, Sweden) in the transmission mode. The XANES (X-ray Absorption Near Edge Structure) spectra of powder samples were measured around the Yb- L_{III} edge at room temperature, 160 and 80 K. Energy resolution of the double-crystal Si (111) monochromator (detuned to reject 50% of the incident signal in order to minimize harmonic contamination) with a 0.5 mm slit at high energies was about 1×10^{-4} .

3. Results and discussion

The new polymorph of YbAg $_2$ with MgZn $_2$ (C14) structure was obtained by melting of the constituent materials at 5 GPa. The new phase of YbAg $_2$ forms golden-pink brittle polycrystals with a metallic luster. In an inert atmosphere at normal pressure and temperature this phase can exist for a long time without any change. It crystallizes in the hexagonal structure ($P6_3/mmc$ space group, № 194, $Z=4$) with the lattice constants $a = 5.68153(3)$ Å and $c = 9.31995(7)$ Å and the unit cell volume $V = 260.54(3)$ Å 3 ($V = 275.186$ Å 3 [2] for the ambient pressure phase with a structure of CeCu $_2$ – $Imma$, $Z=4$). The X-ray diffraction patterns in Fig. 1 confirm the hexagonal Laves phase. The X-ray analysis yielded the lattice constants a, c , coordinates and occupancies of Yb and Ag atoms, that are listed in Table 1. During the Rietveld refinement isotropic displacement temperature parameters (U_{iso} , Å 2) were fixed at the values given in Table 1. Occupancy of Ag(1) atom in 2a position was fixed at 100% level and occupancies of Yb and Ag(2) atoms were refined relative to it.

Fig. 1. Observed (• red) and calculated (• black) X-ray powder diffraction patterns of YbAg₂ (C14) and the difference between them (• blue line at the bottom). Green dashes (|) show positions of Bragg peaks. Two small admixture peaks (2 θ =30.44° and 32.07°) may be ascribed to the presence of Yb₃O₄ and NaCl respectively. Inset shows the crystal structure of YbAg₂ (C14) at room temperature.

Table 1. YbAg₂, Hexagonal $P6_3/mmc$, $a = 5.68153(3)$ Å, $c = 9.31995(7)$

Atoms	Site	x	y	z	$U_{iso}, \text{\AA}^2$	Occupancy,
Yb	4f	1/3	2/3	0.06396(7)	0.00655	0.934(3)
Ag(1)	2a	0	0	0	0.01158	1.000
Ag(2)	6h	-0.16763(4)	-0.33526(4)	1/4	0.01747	1.000(3)

$$\chi^2 = 3.19 \quad R_p = 2.35 \% \quad R_{wp} = 3.51 \% \quad \text{Bragg } R\text{-factor} = 7.03 \%$$

It should be noted that for copper (which is the element of the same IB group as silver) a combination of *ab initio* total-energy calculations and high-pressure x-ray diffraction experiments has been used to study the phase stability of YCu₂ compound and the origin of the change of the structure between the neighboring elements Cu (YCu₂: orthorhombic CeCu₂- type structure) and Ni (YNi₂: defect superstructure of cubic Laves phase MgCu₂-type (C15)) [7]. *Ab initio* calculations confirmed that at an ambient pressure for YCu₂ the CeCu₂ structure is stable while for YNi₂ the C15 structure is energetically favorable. The important difference between YNi₂ and YCu₂ is that the Ni 3d band is not completely filled and has a much stronger overlap with the Y 4d band. Moreover the *ab initio* calculations for YCu₂ show that there might be a phase transition from the CeCu₂ to the C15 structure at approximately 28 GPa [7]. Authors of Ref. [8] performed high-pressure x-ray diffraction experiments on YCu₂ using argon as the pressure transmitting medium. Their experiments showed that CeCu₂ structure is stable at least up to the highest attained pressure of 35 GPa in contrast to an earlier calculations [7]. This observed disagreement between the experiments and the *ab initio* calculations was attributed [8] to an extremely high sensitivity of the crystal structure to non-hydrostatic compression, which together with a possible kinetic frustration is the main reason for the suppression of the transition to the energetically favorable MgCu₂-type structure. Indeed, it was found [9] that at high pressure (8 GPa) and high temperature ($T \approx 1600$ °C), the compound YbCu₂ crystallizes in the hexagonal Laves phase (type MgZn₂).

L_{III} - Yb absorption edge at 80K is shown in Fig. 2. It is apparent, that the spectrum consists of two contributions - Yb²⁺ and Yb³⁺ in spite the fact that the components in the spectra are relatively broad and overlap significantly with each other. Each of these features reflects the distribution of unoccupied Yb 5d states, located nearby the Fermi level and probed by allowed dipole 2p-5d transition. The valence of YbAg₂ was determined by fitting of XANES spectrum using analytical functions. The experimental spectra for all temperatures are well reproduced by the calculation with the Yb mean valence of +2.8, which is obtained from the weight ratio between Yb²⁺ and Yb³⁺ components. Therefore, we observe no changes in Yb valence in the temperature range 80-300 K.

Fig.2. XANES spectrum of YbAg₂ measured at the L_{III} - Yb absorption edge at 80K. The observed spectrum presented with open circles is fitted using two sets of Lorentzian and arctan functions for Yb²⁺ and Yb³⁺ as shown by green and blue lines, respectively. The red line is the fitting curve.

Temperature dependence of the electrical resistivity of YbAg₂ is shown in Fig. 3. The dependence is nonlinear, typical for many intermetallic rare-earth compounds. The low value of RRR = 2.1 indicates the presence of defects, which are formed presumably in this polycrystalline material in the process of rapid cooling of the melt at high pressure. At low temperature the dependence $\rho(T)$ can be approximated by the relation $\rho(T) = \rho_0 + AT^2$ typical for the Fermi liquid. This dependence is shown in the insert in Fig. 3.

Fig.3. Temperature dependence of the electrical resistivity of YbAg₂.

The temperature dependence of the specific heat of YbAg₂ $C(T)$ is shown in Fig.4. The dependence $C(T)/T$ vs T^2 below ~14 K is presented in Fig.5. The most prominent feature of these dependences is the presence of a broad specific heat anomaly which gradually develops below ~6 K and produces the substantial increase of C/T (up to 250 mJ/mol-K² at 0.5 K). The appearance of a long range magnetic order below 0.5 K can be discarded as the specific heat $C(T)$ itself continues to decrease down to the lowest temperature of our measurements (0.5 K).

Fig.4. Temperature dependence of the specific heat of YbAg₂. Insert – enlarged low temperature part.

Fig.5. The dependence of C/T of YbAg₂ vs the square of temperature. The line is a linear fit of the data in the 7-14 K region.

Note, that the appearance of a stable long range magnetic order at low temperature requires the valence of Yb ion to be +3 [9, 10] which is not the case in YbAg₂. The most probable reason of the specific heat anomaly is the presence of spin fluctuations at low temperature which may appear when the valence approaches the +3 value on cooling. Very similar anomaly of the specific heat was observed by Shah et al. [10] in Yb₂Al_{1-x}Mg_xSi₂ system. Variation of x from 0 to 1 produces the evolution of the system from a spin fluctuation state ($x=0$) to a magnetically ordered state ($x=1$) with $T_N = 9.5$ K. Above ~ 7 K the dependence $C(T)/T$ vs T^2 is linear (Fig.5) and one can calculate the electronic specific heat coefficient $\gamma = 12.9$ mJ/mol-K² from the intercept with C/T axis and the Debye temperature $\Theta_D = 156.4$ K from the slope of this linear dependence. This value of γ is in good agreement with that (12.3 mJ/mol-K²) calculated from the Kadowaki-Woods (KW) relation $A/\gamma^2 = R_{KW} = 1 \times 10^{-5} \mu\Omega \cdot \text{cm} \cdot (\text{K} \cdot \text{mol/mJ})^2$ [11] with the use of $A = 1.51 \times 10^{-3} \mu\Omega \cdot \text{cm/K}^2$ found from resistivity measurements on our sample of YbAg₂. Kontani [12] based on the Fermi liquid theory suggested that the ratio of A/γ^2 , so far considered to be unique and independent of materials, does depends on the value of degeneracy of quasiparticles N . In solids, N can vary due to the competition between the crystal-field splitting Δ and the Kondo temperature T_K . The value of A/γ^2 is then deduced as [13] $A/\gamma^2 \approx 1 \times 10^{-5} / [1/2 N(N-1)] \mu\Omega \cdot \text{cm} \cdot (\text{K} \cdot \text{mol/mJ})^2$. For the case of $N=2$, this formula gives the KW relation and this is consistent with the situation $T_K < \Delta$. We can then estimate a value of T_K by using $T_K = (R \ln N) / \gamma$ [14]. For the high pressure phase of YbAg₂ the Kondo temperature T_K is equal to 447 K.

Fig. 6 presents the temperature dependence of the magnetic susceptibility measured in the field of 1000 Oe. The susceptibility is weakly dependent on temperature down to 50 K. At further lowering of temperature the value of the susceptibility increases sharply. This may be due to a tiny amount of Yb⁺³ ions ($\sim 0.26\%$) which act as magnetic impurities and at low temperatures the susceptibility is Curie-Weiss-like $\chi(T) = C/(T+\theta)$, where C is the Curie constant and θ is the Curie-Weiss temperature. From a phenomenological point of view, a Fermi-liquid picture with enhanced spin fluctuations could account for magnetic properties of intermediate-valence compounds [15], wherein the low-temperature susceptibility of a nearly magnetic fermion system varies like $\chi_P(T) = \chi_P(0)[1+a(T/T_{sf})^2]$ for $T < T_{sf}$ (T_{sf} is the spin-fluctuation temperature) with $\chi_P(0) \sim 1/T_{sf}$ and a is a number of the order of 1, which can be negative or positive. Since in YbAg₂ compound the ytterbium ion has a valence equal to 2.8 and a Fermi-liquid behavior of $\rho(T) = \rho_0 + AT^2$ was found, for the description of the experimental temperature dependence of susceptibility we used the

expression $\chi(T) = C/(T + \theta) + \chi_P(T)$. As a result, we obtained the following values of the fitting parameters: $C = 2 \cdot 10^{-5} \text{ K} \cdot \text{cm}^3/\text{g}$, $\theta = 1.66 \text{ K}$, $\chi_P(0) = 5.87 \cdot 10^{-7} \text{ cm}^3/\text{g}$, $a = -1.19$, $T_{sf} = 908.4 \text{ K}$. The result of the fit is shown as a red line in Fig. 6 and gives a good approximation of experimental data (circles). We thus see that the T^2 term is needed for adequate presentation of the temperature dependence of susceptibility of YbAg_2 . This gives a strong support to the Fermi-liquid picture in intermediate-valence compound YbAg_2 .

Fig.6. Temperature dependence of the magnetic susceptibility of YbAg_2 . The line is the fit of the data as described in the text.

4. Conclusions

We have successfully synthesized the new phase of YbAg_2 using high-pressure and high-temperature reaction of Yb and Ag metals. The high-pressure phase of YbAg_2 is the first example where silver forms a compound with a heavy rare-earth element which has the hexagonal Laves phase structure of MgZn_2 type. The XANES analysis showed that the average valence state of Yb is +2.8. The T^2 term was found in the temperature dependences of $\rho(T)$ and $\chi(T)$ which gives a strong support to the Fermi-liquid picture in the intermediate-valence compound YbAg_2 . The electronic specific heat coefficient $\gamma = 12.9 \text{ mJ/mol} \cdot \text{K}^2$. Analysis of the Kadowaki-Woods relation gives a low value of the degeneracy $N = 2$.

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