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High pressure synthesis of a new phase of $YbAg_2$: Structure, valence of Yb and properties

A.V. Tsvyashchenko [a, *], A.P. Menushenkov [b], V.A. Sidorov [a], A.E. Petrova [a], L.N. Fomicheva [a], O.V. Chernysheva [b], Yu.B. Lebed [c, d], S.N. Axenov [c], S.L. Bud'ko [e], Liling Sun [f, g], Zhongxian Zhao [f, g]

[a] Vereshchagin Institute for High Pressure Physics, Russian Academy of Sciences, 142190 Moscow, Troitsk, Russia
[b] Moscow Engineering Physics Institute, Kashirskoe shosse 31, 115409 Moscow, Russia
[c] Institute for Nuclear Research, Russian Academy of Sciences, 142190 Moscow, Troitsk, Russia
[d] Moscow Institute for Physics and Technology, Dolgoprudny, Moscow Region 141700, Russia
[e] Ames Laboratory and Department of Physics and Astronomy, Iowa State University, Ames, IA 50011, USA
[f] Institute of Physics and Beijing National Laboratory for Condensed Matter Physics, Chinese Academy of Sciences, Beijing 100190, China
[g] Collaborative Innovation Center of Quantum Matter, Beijing, 100190, China

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ABSTRACT

The new phase of $YbAg_2$ was obtained using high-pressure and high-temperature reaction. $YbAg_2$ crystallizes in the $MgZn_2$ structure (the space group $P6_3/mmc$ space group, No 194) with $a = 5.68153(3)$ Å and $c = 9.31995(7)$ Å and the unit cell volume $V = 260.54(3)$ Å^3. 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 $Yb^{3+}(4f^{13})$ state rather than to the divalent nonmagnetic $Yb^{2+}(4f^{14})$ state.

It is known that at ambient pressure the compound $YbAg_2$ in which ytterbium ion is divalent and non-magnetic crystallizes in the orthorhombic structure of the $CeCu_2$ 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 $T \approx 1450\,^\circ C$ (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.

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* Corresponding author.
E-mail address: tsvyash@hppi.troitsk.ru (A.V. Tsvyashchenko).

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Powder XRD pattern of the compound was collected on HUBER (G670) diffractometer with Cu $K_{\alpha 1}$ radiation in transmission mode, at 2θ step 0.005° in the angular range from 4 to 95° at room temperature. Crystal structure was investigated by Rietveld full-profile analysis of XRD pattern, using Fullprof [5] and WinPLOTR [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 ^{3}He 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, No 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.

Table 1
$YbAg_2$, Hexagonal $P6_3/mmc$, $a = 5.68153(3)$ Å, c = 9.31995(7).

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

$\chi^2 = 3.19$ $R_p = 2.35\%$ $R_{wp} = 3.51\%$ Bragg R-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 YCu_2 compound and the origin of the change of the structure between the neighboring elements Cu (YCu_2: orthorhombic $CeCu_2$-type structure) and Ni (YNi_2: defect superstructure of cubic Laves phase $MgCu_2$-type (C15)) [7]. *Ab initio* calculations confirmed that at an ambient pressure for YCu_2 the $CeCu_2$ structure is stable while for YNi_2 the C15 structure is energetically favorable. The important difference between YNi_2 and YCu_2 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 YCu_2 show that there might be a phase transition from the $CeCu_2$ to the C15 structure at approximately 28 GPa [7]. Authors of Ref. [8] performed high-pressure x-ray diffraction experiments on YCu_2 using argon as the pressure transmitting medium. Their experiments showed that $CeCu_2$ 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

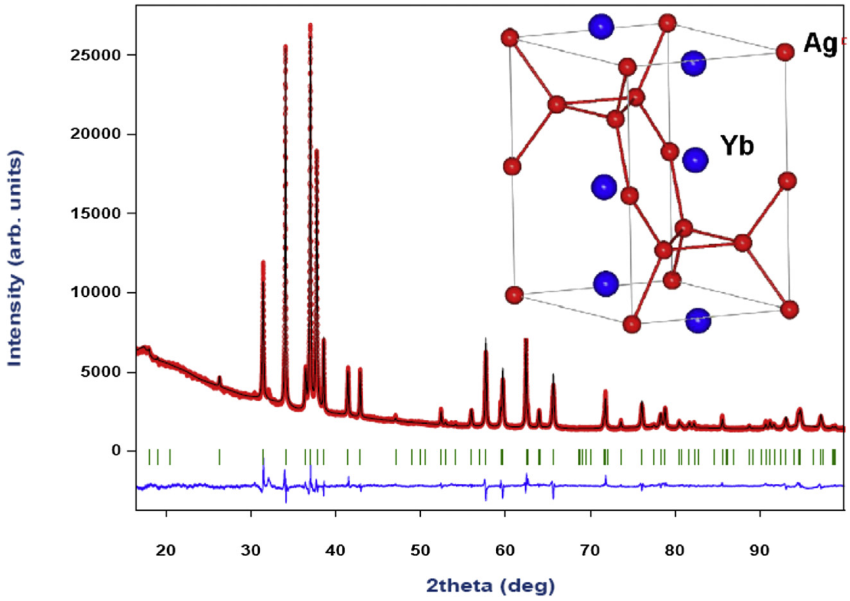

Fig. 1. Observed (● red) and calculated (● black) X-ray powder diffraction patterns of $YbAg_2$ (C14) and the difference between them (● blue line at the bottom). Green dashes (|) show positions of Bragg peaks. Two small admixture peaks (2θ = 30.44° and 32.07°) may be ascribed to the presence of Yb_3O_4 and NaCl respectively. Inset shows the crystal structure of $YbAg_2$ (C14) at room temperature. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)