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## Elements of the Phase Diagram of YbInCu<sub>4</sub>

To clarify how the valence transition temperature of YbInCu<sub>4</sub> is connected with the composition of the grown crystals, we investigated the phase diagram. Since elements of the liquidus curve of the system Yb-In-Cu were already known we focused on the solidus curve in the surrounding of the valence changing YbInCu<sub>4</sub>. Bridgman-technique for crystal growth was used. The composition of the solidified crystals was determined by means of wavelength-dispersive X-ray analysis. The valence transition temperature is measured via the lattice constant by low temperature X-ray diffraction.

Results are, that the assumed exchange of Yb and In, which is indicated in the formula Yb<sub>x</sub>In<sub>2-x</sub>Cu<sub>4</sub> seems to be not correct. Not the quasi-binary section for constant Copper content should be used, but one for constant Ytterbium content. Starting compositions with an excess of Ytterbium lead to the substitution of Indium by Copper. The valence transition temperature of these crystals is shifted from 40K to 70K.

Keywords: YbInCu<sub>4</sub>, valence transition, phase diagram, Bridgman-method

### 1. Introduction

In 1986 Felner and Nowik (FELNER et al.) reported a first order valence transition of a compound which was later determined by Kojima (KOJIMA et al.) as YbInCu<sub>4</sub> where the Yb-ion changes its valence from 3<sup>+</sup> to an average value of 2.9<sup>+</sup>. This valence transition can be observed at normal pressure and occurs between 40K and 80K. Before 1994 all measurements were made on polycrystalline samples. Often two subsequent anomalies could be detected. A very sharp change at 40K and sometimes a smaller one nearby 70K. In 1994 Kindler et. al. have grown the first single crystals using Bridgman technique (KINDLER et al.). Measurements of the temperature dependence of the resistivity, the lattice constant and the elastic properties show mostly a valence transition at 70K. Recently single crystals were grown by Lawrence and Sarrao (LAWRENCE et al. 1996, SARRAO et al.) using a Cu-In-Flux. Further they annealed polycrystalline samples which were cooled slowly or quenched rapidly from melting temperatures. They found that the slowly cooled samples have a larger portion of the “70K-phase“ as other samples. The sharpest valence transition is measured on flux grown crystals at 40K. Inelastic neutron scattering results (LAWRENCE et al. 1997) show that these crystals are highly ordered concerning the site occupation of the elements in the AuBe<sub>5</sub>-structure in which YbInCu<sub>4</sub> crystallizes. Fischbach (FISCHBACH et al.) carried out thermoanalytical investigations with different compositions. The results showed, that for crystals grown from starting compositions with significant Ytterbium-deficiency in

comparison to the stoichiometric composition YbInCu<sub>4</sub> a valence change at 40K occurs. From a critical content of about  $0.8 < x < 0.9$  of Yb to higher contents, with respect to the formula Yb<sub>x</sub>In<sub>2-x</sub>Cu<sub>4</sub>, the effect is seen at about 70K. This means that within the System Yb-In-Cu more than one valence changing phase with AuBe<sub>5</sub> type structure and composition near YbInCu<sub>4</sub> exists. The exact compositions of the crystals were not known.

Our intention is to analyze the solidus curve in the Yb-In-Cu phase diagram in the relevant surrounding of YbInCu<sub>4</sub> to find out whether there are compositional differences between the 70K- and the 40K-samples. Till now no informations about the solidus curve are available. Following the first assumptions of Felner and Nowik about the possibility of an exchange of Yb and In, which is expressed by the formula Yb<sub>x</sub>In<sub>2-x</sub>Cu<sub>4</sub>, we have grown single crystals using different starting compositions including the range from  $x=0.7$  to  $x=1.3$ .

## 2. Experimental Setup

### 2.1. Crystal Growth

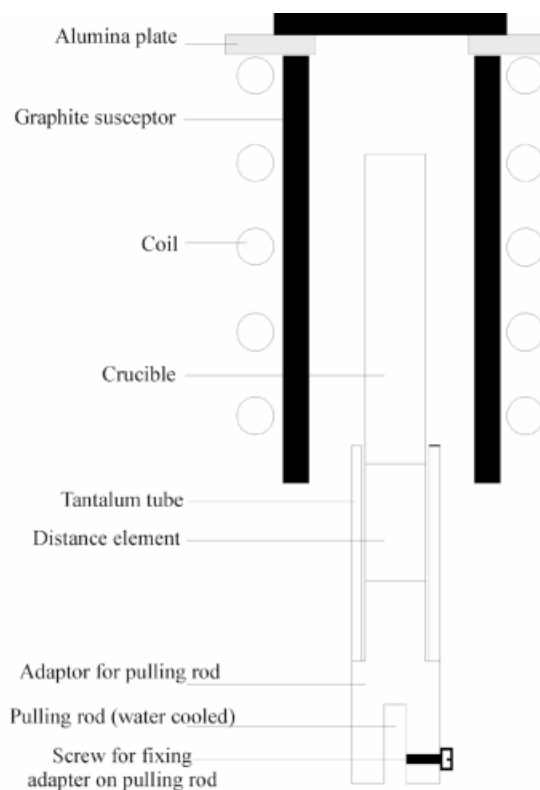


Fig. 1: Crucible arrangement in the furnace for Bridgman crystal growth

For growth a tantalum crucible was used which was closed gas tight under Argon atmosphere by a tool described by Fischbach (FISCHBACH). The crucible was indirectly heated by a high frequency field using a graphite susceptor (Fig. 1). The Bridgman technique was used under Argon atmosphere. The velocity of crystal growth differs between

1.1mm/h and 3mm/h. The maximum temperature of the susceptor is monitored by a pyrometer and held between 1200°C and 1300°C. The melting point of YbInCu<sub>4</sub> is approximately 1000°C.

## 2.2. Characterization methods

After growth the crucibles are opened with spark erosion. First impressions of the formation of secondary phases are taken by optical polarisation microscopy. For more precise analysis of the distribution and the composition of these phases a scanning electron microscope (Zeiss DSM940A) equipped with an energy dispersive X-ray analysis system (EDAX PV9800) is used. Parts with different valence transition temperatures are compared concerning their composition by means of wavelength dispersive X-ray analysis (Microspec 3PC) in combination with standards. The valence transition temperature is measured via the detection of the temperature dependence of the lattice constant. The X-ray powder diffractometer (Siemens D500) is equipped with a closed cycle helium refrigerator (Lake Shore). The usable temperature range comprises the interval between 10K and 300K.

## 3. Characterization

### 3.1 Phase Diagram

Single crystals up to a size of 4x4x4mm<sup>3</sup> using a crucible diameter of about 6mm could be grown. The starting composition of Yb<sub>1.1</sub>In<sub>0.9</sub>Cu<sub>4</sub> shows the lowest content of secondary phases of about 2%. Beginning with compositions more far from the stoichiometric composition leads to inclusion of other phases and to bad crystallization of the material, examples are Yb<sub>1.3</sub>In<sub>0.7</sub>Cu<sub>4</sub> and Yb<sub>0.7</sub>In<sub>1.3</sub>Cu<sub>4</sub>.

As a result of the the analysis of the crystallized material a slight shift of the composition along the crucible axis could be clearly established. In each case one measurement is taken near the bottom, in the middle and in the highest region of the crucible. The results are shown in Fig. 2. Obviously, the solidus curve did not follow the commonly chosen section of constant Copper content. The solidus compositions follow very well the section for constant Ytterbium. This means, the ratio of built-in Copper and Indium varies with the starting composition.

Starting compositions with excess of Ytterbium lead to the growth of crystals with excess of Copper and Indium deficiency. These results shown in Fig. 2 imply a very narrow "ridge" in the solidus curve. The summit, that means the highest melting point, is located near YbIn<sub>0.8</sub>Cu<sub>4.2</sub>. This "ridge" seems to end with a steep slope near the stoichiometric composition. This explains, that the flux growth method, applied by Lawrence (LAWRENCE et. al. 1996) leads to homogenous crystals near the stoichiometric composition. They had grown crystals out of this quasi-binary section in the Copper-deficient part.

### 3.2 Crystal composition and phase transition temperature

The measured samples show a systematic behaviour. Referring to Fig. 3 a low phase transition temperature T<sub>VF</sub> near 40K could be measured for the samples which were grown from Ytterbium-deficient melts. Following the "ridge" to higher Copper contents T<sub>VF</sub>

increases. With further increase of the Cu-concentration the valence transition becomes less pronounced. At YbCu<sub>5</sub> no valence transition was observed (HE et. al.).

A remaining question concerns the occupation of the Be(I) and Au-sites of AuBe<sub>5</sub>-structure by Ytterbium-, Indium- and Copper-Ions. The results concerning the relation between microstructure and valence transition will be published in the near future.

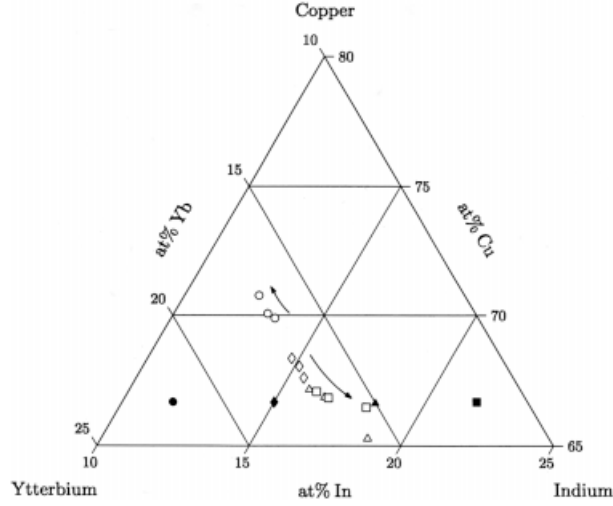


Fig. 2: Corresponding liquidus and solidus compositions. The blank symbols denotes the composition with sequence of solidification concerning the starting compositions which are represented by filled symbols.

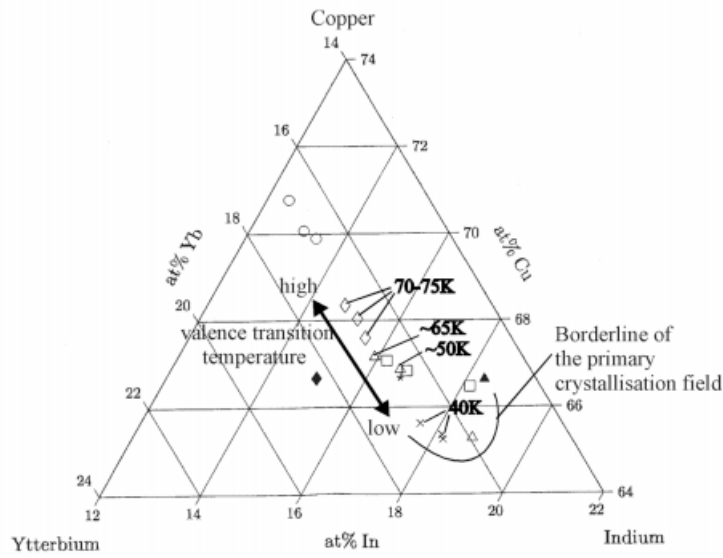


Fig. 3: Crystal compositions and corresponding valence transition temperatures. Notation as in Fig. 2.

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