Mixed-valence transition in $YbInCu_4$

B. Kindler, D. Finsterbusch, R. Graf, F. Ritter, W. Assmus, and B. Lüthi
Physikalisches Institut, Universität Frankfurt, D-60054 Frankfurt, Germany
(Received 23 February 1994)

We present single-crystal data of mixed-valent $YbInCu_4$ including a description of the single-crystal-growth procedure. Many of the data, such as magnetic susceptibility, electrical resistivity, and lattice constant, are similar to previously published polycrystalline data although the mixed-valent transition at 66.9 K is sharper than in the latter case. In addition, elastic-constant data are presented which exhibit a pronounced softening of the bulk modulus and the Poisson ratio at T_a.

I. INTRODUCTION

In intermediate valence fluctuation compounds one usually observes phase transitions from a semiconducting or metallic phase to a mixed-valence metallic phase as a function of pressure or stoichiometry.[1] To our knowledge no such transition has been observed at ambient pressure as a function of temperature for a stoichiometric compound with the exception of $YbInCu_4$. This compound has been studied in its polycrystalline form with a variety of techniques.[2,3] It was found that at atmospheric pressure it undergoes an isostructural transition at ~ 50 K. The resulting valence change was rather small, Yb^{3+} in the high-temperature phase changing to $Yb^{2.9+}$ in the low-temperature phase.

In this paper we describe the growth of single crystals of this compound and present experimental results on lattice constants, magnetic susceptibility, electrical resistivity, and elastic constants on monocrystalline $YbInCu_4$. These measurements enable us to characterize the valence fluctuations as a function of temperature. The results are briefly the following: (a) At the phase transition at $T_a = 66.9$ K the lattice constant changes abruptly by about 0.13% without any splitting of Bragg reflections, indicating an isostructural transition. (2) The magnetic susceptibility is very similar to the results of polycrystalline specimens. (3) The electrical resistivity shows also a steplike behavior at T_a with a residual resistivity of 15.1 $\mu\Omega$ cm at low temperatures. (4) The most important results for the elastic constants are a strong softening of the bulk modulus c_B of 43% at the transition temperature and a change in the Poisson ratio of 30%. These results will be discussed for a model of valence fluctuations.

II. CRYSTAL GROWTH

For the growth of $YbInCu_4$ single crystals we start with Yb (4*N*, Universal Matthey), In (5*N*5), and Cu (6*N*) materials. The Yb is delivered in sublimed needles and has a rough and very large surface. It turned out to be of particular importance to purify the Yb, since very small amounts of residual oxygen can affect the Ta crucible and thus cause leaks. We therefore melt our Yb in a cold crucible to a compact form and remove the oxidized surface mechanically. Thereafter stoichiometric amounts of Yb, In, and Cu are placed in a Ta tube of 10 mm in diameter and a wall thickness of 1 mm. Then both ends are arc-welded under argon atmosphere. This sealing is necessary because of the high vapor pressure of ytterbium (approximately 5×10^3 Pa) at the melting temperature of the compound (about 1000 °C), which we determined with differential thermal analysis.

The crystals are grown in an ADL-puller under argon with Bridgman technique. The Ta tube contains a cone-shaped Ta insert in order to ensure a good seed selection. The crucible is heated indirectly by means of a graphite susceptor in a rf coil. The whole crucible is heated under argon atmosphere up to about 1100 °C and, after a homogenization period of about half an hour, lowered with respect to the susceptor with a velocity of ~ 2 mm/h.

After the growth process the crucible is opened with an abrasive wheel. Single crystals with a size of $(2\times4\times4)$ mm^3 are cut from the charge by means of a diamond saw and are orientated with x-ray Laue technique. The samples are characterized with a scanning electron microscope together with electron probe microanalysis to ensure that the material has the correct composition and impurities (e.g., from the crucible) are not present. In addition the structure and the variation of the lattice constant as a function of temperature down to 10 K are investigated by x-ray powder diffraction.

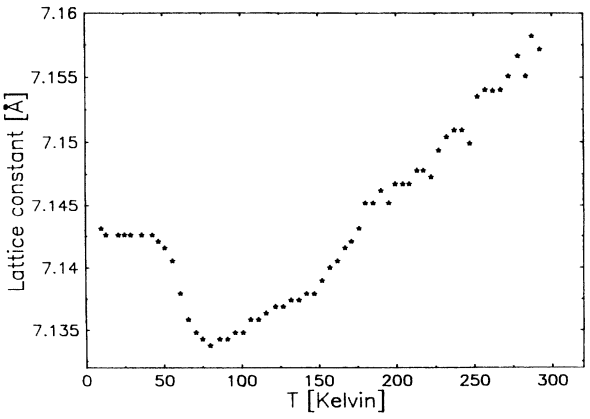

FIG. 1. Lattice constant a as a function of temperature.

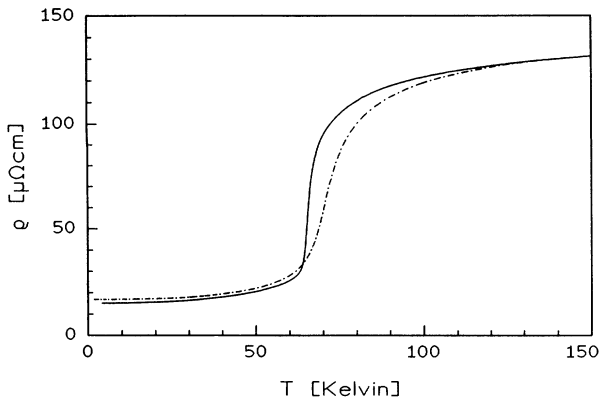

FIG. 2. Electrical resistivity as a function of temperature for monocrystalline (full line) and polycrystalline (dotted line) $YbInCu_4$.

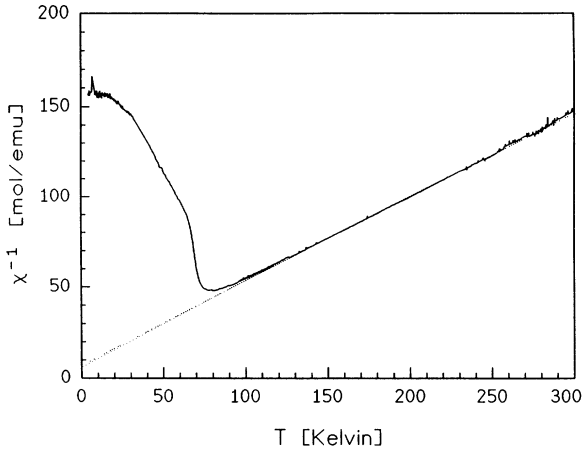

FIG. 3. Inverse susceptibility as a function of temperature. Dotted line gives extrapolation for Curie-Weiss plot.

$YbInCu_4$ crystallizes in a C15b-type structure ($AuBe_5$).[4] In order to ensure that no cubic-tetragonal or cubic-orthorhombic transition occurs we investigated the temperature dependence of the (422)-Bragg reflex with x-ray powder diffraction. In Fig. 1 we show the lattice constant a as a function of temperature. The transition can be seen clearly at around 70 K.

III. ELECTRICAL RESISTANCE

In Fig. 2 we show our measurements of the electrical resistivity as a function of temperature for the single-crystal sample. The resistance exhibits a more pronounced step than our own data on polycrystalline material which are also shown in Fig. 2. The step is also sharper than the data of Ref. 2 where a slight multistep function can be discerned. The step at T_a is about six times the low-temperature resistivity which amounts to 15.1 $\mu\Omega$ cm. The temperature derivative of the electrical resistivity has a maximum very close to the assumed T_a.

The longitudinal magnetoresistance at 4 K (not shown) increases approximately quadratically by about 7% up to 11 T. No trend to saturation in high fields can be seen.

IV. MAGNETIC SUSCEPTIBILITY

In Fig. 3 we plot the inverse susceptibility versus temperature. The high-temperature data exhibit a strict Curie-Weiss law from 100 to more than 300 K. The Curie constant gives a magneton number of $\mu_{\text{eff}}=4.64\mu_B$ very close within limits of our calibration error to the valence of the free ion ($4.54\mu_B$) and in agreement with literature values.[2] The linear extrapolation (Fig. 3) gives a paramagnetic Curie temperature of $\Theta=-15$ K as in Ref. 3. The low-temperature part of the susceptibility does not show an upturn like previous data,[2,3] the latter probably arises from magnetic impurities. The relevant data are listed in Table I.

V. ELASTIC CONSTANTS

In Fig. 4 we give an overview of the temperature dependence of the three elastic constants for the cubic $YbInCu_4$: $c_L=(c_{11}+c_{12}+2c_{44})/2$, $(c_{11}-c_{12})/2$, and c_{44}. These results were obtained from relative frequency measurements[5] and absolute sound velocity measurements. The absolute elastic constants are listed in Table I together with other relevant material parameters of $YbInCu_4$ The thermal expansion is rather large in this compound,[3] e.g., at the transition temperature T_a $\Delta a/a\approx 0.1\%$. The corresponding sound velocity changes in the vicinity of T_a are even more than an order of magnitude larger. Therefore length change corrections still have a negligible effect on the elastic constants at least for c_L.

It is seen that the shear waves exhibit a steplike anomaly at T_a whereas the longitudinal mode c_L shows, in addition to the steplike anomaly, a very strong softening of about 27% at T_a. The inset of Fig. 4 shows the detailed temperature dependence of c_L in the vicinity of T_a giving a value of $T_a=66.9$ K. From these elastic constants we can deduce the bulk modulus $c_B=(c_{11}+2c_{12})/3$ and the

TABLE I. Physical properties of $YbInCu_4$.

Space group $F\bar{4}3m$,	4 formula units per unit cell	
Density ($T=300$ K, $a=7.16$ Å)	$\rho=9.81$ g/cm^3	
Specific heat	$\gamma=22.3$ mJ/(mol K^2)	Ref. 2
Magn. susc. ($T=4$ K)	$\chi=6.37\times10^{-3}$ emu/mol	
Residual resistivity	$\rho_0=15.1$ $\mu\Omega$ cm	
Elastic constants for $T=175$ K	(in 10^{11} erg/cm^3)	
$c_{11}=17.20$	$c_{12}=8.29$	$c_{44}=6.57$
$T_a=66.9$ K	$\Theta=-15$ K	$\mu=4.64\mu_B$

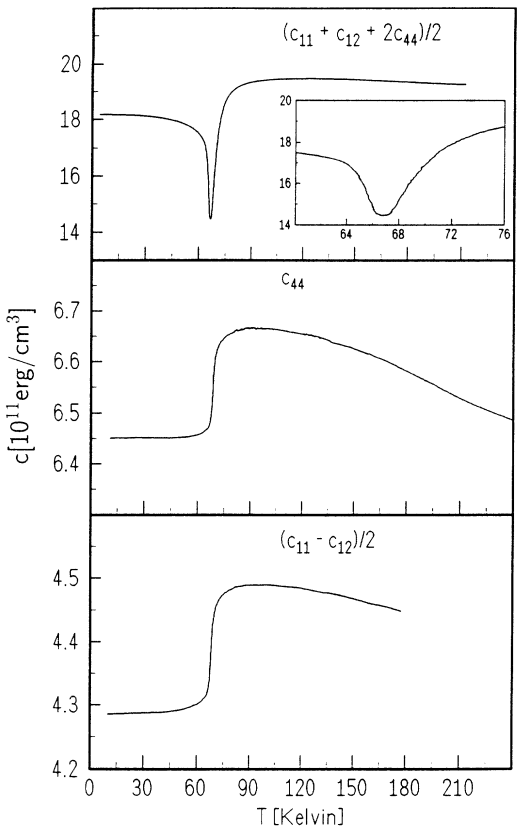

FIG. 4. Elastic constants as a function of temperature. Inset gives $c_L(T)$ around T_a.

Poisson ratio $\nu=c_{12}/(c_{11}+c_{12})$, the quantities relevant for valence fluctuations.[6] These two quantities are shown in Fig. 5. They exhibit both pronounced anomalies at the phase transition T_a. The softening for c_B and ν amounts to 43 and 30 %, respectively.

VI. DISCUSSION

There are various Yb-based mixed-valent compounds such as $YbAl_2$, $YbAl_3$, YbB_{12}, and YbCuAl. In all these compounds with the exception of $YbAl_2$ the Yb valence changes from 3+ to 2.9+, a relatively small change. This is the case also for $YbInCu_4$.[2,3] As pointed out above, the valence transition occurs in this case as a function of temperature already at ambient pressure. The anomalies in the different physical quantities are rather sharp at T_a. For example, the susceptibility changes abruptly at this temperature in contrast to say YbB_{12}.[7] But especially the longitudinal elastic mode c_L has a very deep and narrow minimum which enables one to define T_a very accurately. This is in contrast to other mixed-valent compounds which do not exhibit phase transitions as a function of temperature such as $CeSn_3$, $CePd_3$, SmB_6,[9] etc. In these latter compounds a hybridization gap explains the thermodynamic properties adequately.[7,8] In the case of $YbInCu_4$ the resistance change across the transition indicates that a gap can only exist for parts of the Fermi surface.

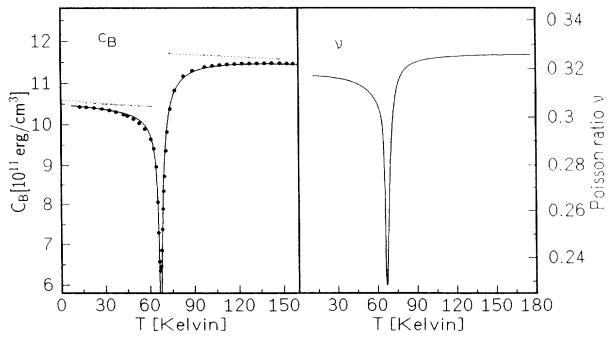

FIG. 5. Temperature dependence of the bulk modulus c_B and the Poisson ratio ν. For c_B the full circles denote the experimental values, the dotted lines the background c_B^0, and the full lines the calculated fit using Eq. (2). For ν the full line is calculated from the experimental data.

In order to understand the mechanism of this valence transition a comparison can be made to a model for the α-γ transition in metallic cerium.[10] Although this valence fluctuation model is no longer used for Ce, its ingredients can be applied to our valence transition in $YbInCu_4$. The authors of Ref. 10 calculate magnetic susceptibility and f-electron occupation for a model where the f level lies above the Fermi energy. The high-temperature phase is magnetic through the occupation of this f level. The phase transition is driven through the entropic loss of magnetic degrees of freedom $2J+1$. Since this model gives a valence change from 1 to 0, the f-level occupancy disappears for $T=0$ in contrast to $YbInCu_4$, where the valence change is only from 3 to 2.9.

The elastic constants for an intermediate valence fluctuating compound can be described simply by a Landau model. The order parameter, the normalized $4f$ occupancy can be related to the volume strain ϵ_V (Ref. 1) because the volume of the single rare-earth ion shrinks if the R^{n+} $(4f^m)$ ion changes to R^{n+1} $(4f^{m-1})$. The corresponding soft mode is the bulk modulus c_B. The other elastic constants having E and T_2 symmetry exhibit step-like functions at T_a and do not couple to the A_{1g} symmetry order parameter. Denoting the order parameter with η the Landau free energy reads

$$F=\alpha(T-T_c)\eta^2+\beta\eta^4+g\epsilon_V\eta\ , \tag{1}$$

where g denotes the strain-order parameter coupling constant and α,β are the Landau coefficients. T_c is the transition temperature without any coupling to the strains. From Eq. (1) one can readily calculate the corresponding elastic constant with the result[11] for $T>T_a$:

$$c_B=c_B^0\frac{T-T_c-(g^2/(2\alpha c_B^0))}{T-T_c}\ . \tag{2}$$

Here c_B^0 is the background bulk modulus as indicated in Fig. 5 (dotted lines). The renormalized transition temperature is $T_a=T_c+g^2/(2\alpha c_B^0)$. A fit of Eq. (2) for the bulk modulus is also shown in Fig. 5 (full lines) with the values of $T_c=66.06$ K and $T_a=66.9$ K. It is seen that $T_c \gg g^2/(2\alpha c_B^0)$ for $YbInCu_4$. The nice fit shows that

indeed c_B is the soft mode and the volume strain proportional to the order parameter. A similar fit (neglecting the possibility of a small first-order transition) can be used for $T < T_a$ with slightly reduced c_B^0 and Eq. (2) is modified in the denominator. The fact that c_L, c_B, and v have lower values in the low-temperature phase (10, 10, and 3% reduction, respectively) indicates the mixed-valence regime with reduced parameters.

As to the other elastic constants $(c_{11}-c_{12})/2$ and c_{44}, the steplike nature of their temperature dependence indicates that they must couple somehow to electronic degrees of freedom but symmetry considerations show that they cannot couple directly to the square of the A_{1g} order parameter. A microscopic model is needed to fully understand the energetics of this temperature-dependent valence phase transition.

ACKNOWLEDGMENTS

This research was supported by the DFG through SFB 252. We acknowledge interesting discussions with L. L. Hirst, V. Zlatic, and A. C. Hewson.

[1]For reviews on valence fluctuation phenomena see, e.g., J. M. Lawrence, P. S. Riseborough, and R. D. Parks, Rep. Prog. Phys. **44**, 1 (1981); A. C. Hewson, J. Magn. Magn. Mater. **12**, 83 (1979); C. M. Varma, Rev. Mod. Phys. **48**, 219 (1976).

[2]I. Felner, I. Nowik, D. Vaknin, U. Potzel, J. Moser, G. M. Kalvius, G. Wortmann, G. Schmiester, G. Hilscher, E. Gratz, C. Schmitzer, N. Pillmayr, K. G. Prasad, H. de Waard, and H. Pinto, Phys. Rev. B **35**, 6956 (1987).

[3]H. Müller, E. Bauer, E. Gratz, K. Yoshimura, T. Nitta, and M. Mekata, J. Magn. Magn. Mater. **76&77**, 159 (1988).

[4]K. Kojima, H. Hayashi, A. Minami, Y. Kasamatsu, and T. Hihara, J. Magn. Magn. Mater. **81**, 267 (1989).

[5]B. Lüthi, G. Bruls, P. Thalmeier, B. Wolf, D. Finsterbusch, and I. Kouroudis, J. Low Temp. Phys. **95**, 257 (1994).

[6]B. Lüthi, J. Magn. Magn. Mater. **52**, 70 (1985).

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

[8]R. Takke, M. Niksch, W. Assmus, B. Lüthi, R. Pott, R. Schefzyk, and D. K. Wohlleben, Z. Phys. B **44**, 33 (1981).

[9]S. Nakamura, T. Goto, M. Kasaya, and S. Kunii, J. Phys. Soc. Jpn. **60**, 4311 (1991).

[10]R. Ramirez and L. M. Falicov, Phys. Rev. B **3**, 2425 (1971).

[11]B. Lüthi and W. Rehwald, *Structural Transitions I,* edited by K. A. Müller and H. Thomas, Topics in Current Physics, Vol. 23 (Springer-Verlag, Berlin, 1981).