Anomalous Compressibility Associated with First Order Valence Change in YbInCu₄

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Thermal expansion of the YbInCu₄ compound and volume anomaly ω_v associated with a sudden change of Yb valence ν at T_V were measured under pressure up to 10 kbar. Both, the temperature $T_V \approx 40$ K and the anomaly $\omega_v = 0.43$ % decrease under pressure linearly (with slopes $dT_V/dp = -2.2$ K/kbar⁻¹ and $d\omega_v/dp = -0.021$ % kbar⁻¹) up to a critical pressure $p_C \approx 20$ kbar. The compressibility κ increases below T_V , $\kappa = 1.22$ Mbar⁻¹ at 20 K and $\kappa = 0.99$ Mbar⁻¹ at 295 K. A derived pressure change of ν (or f -shell occupation n_f), $d\nu/dp \approx 0.005$ kbar⁻¹, leads to $d \ln V_{Yb} / dn_f \approx 0.15$. [valence fluctuation, thermal expansion, compressibility, rare earth intermetallics]

1. Introduction

During the last years, a great attention has been paid to the study of the YbInCu₄ compound that belongs to a family of mixed-valence systems. Very sudden and pronounced changes of its physical properties, as a sharp volume increase and an abrupt decrease of electrical resistivity and magnetic susceptibility, have been observed at temperature $T_V \approx 40$ K. At the same time, the C15b cubic crystal structure of the YbInCu₄ compound remains stable, unaffected by these significant changes [1-4]. The sudden change of the Yb valence ν (from Yb⁺³ above T_V to an intermediate valence Yb^{+2.9} below T_V) was deduced from the above mentioned measurement, X-ray absorption spectra and Cu nuclear quadrupole resonance study at low temperatures [1-5]. It was accepted that the $4f$ electrons of Yb become suddenly hybridized with conduction d -electrons in YbInCu₄ below T_V . The first-order-like Yb valence change in YbInCu₄ differs in this sense from the known continuous valence transition in pure Yb under pressure [6].

The first-order valence change is accompanied by an anomalous volume expansion with decreasing temperature below T_V . This has been a reason for very intensive pressure study of these phenomena in the last years [2, 7-10]. In this contribution we present the results of the study of the effect of pressure on the volume anomaly in the YbInCu₄ compound based on compressibility and thermal expansion measurements under pressure.

2. Experimental details and Results

The polycrystalline YbInCu₄ compound was prepared by arc melting of the constituent elements. The phase purity was checked by X-ray powder diffraction technique at room temperature. A SQUID magnetometer was used to measure the ac-susceptibility of YbInCu₄ in

the temperature range 5-300 K and to determine the temperature T_V . The real part of the susceptibility χ' drops abruptly at $T_V \approx 40$ K reflecting the transition to the mixed-valence state. The imaginary part of the susceptibility χ'' shows a rapid increase below T_V . It can be related to the noticed decrease of the resistivity and relevant increase of eddy currents in the sample. The temperature dependence of $1/\chi'$ is plotted on Fig. 1. The linear fit of the curve above T_V follows the simple Curie law with Weiss constant $\theta = 0$ and $\mu_{\text{eff}} = 4.41 \mu_B$, very close to the free Yb⁺³ ion magnetic moment ($4.54 \mu_B$). This behaviour of ac-susceptibility verifies the good quality of the studied samples.

Fig. 1. Dependence of $1/\chi'$ vs. T under normal pressure

The compressibility and the thermal expansion of YbInCu₄ were measured by micro-strain gauges (Micro-Measurements Inc., SK-350) in temperature range from 10 K to 300 K. The strain gauges were calibrated using the relevant reference data of compressibility and thermal expansion of silica, Cu and Fe. The pressure experiments were performed in a CuBe cell with fixed

hydrostatic pressure up to 9 kbar. The pressure was measured *in situ* using a manganin pressure sensor.

The linear thermal expansions of the YbInCu₄ and the isostructural LuInCu₄ compounds are compared in Fig. 2 to determine the volume anomaly at T_V and its pressure dependence. (To eliminate the pressure effect on the Yb⁺³ phase above T_V , the curves were shifted to coincide with the LuInCu₄ data at $T > 100$ K.) The increase of volume due to the first-order Yb valence change in the YbInCu₄ compound is $\omega_v = 3\Delta L / L = 0.43$ % under normal pressure (it well agrees with 0.45 %, determined by X-ray diffraction [1,4]) and it decreases with a slope of $d\omega_v/dp = -0.021$ % kbar⁻¹ under increasing pressure.

Fig. 2. Linear thermal expansion of YbInCu₄ vs. temperature under several pressures. A dotted „lattice“ curve represents the thermal expansion of LuInCu₄.

T_V was determined as the temperature of the maximum on the thermal expansion coefficient curve under pressure (see Fig. 3). A linear fit of the pressure shift of T_V gives the value :

$$dT_V/dp = -2.2 \text{ K kbar}^{-1}$$

which is in a good agreement with previous pressure results [2,7-10].

Both parameters $(d\ln\omega_v/dp)^{-1}$ and $(dT_V/dp)^{-1}$ give the same value of the critical pressure $p_C \approx 20$ kbar for a loss of the valence change phenomenon. Using this value of p_C and the relevant increase of the Yb valence in the YbInCu₄ compound, $\Delta v = 0.1$, we can estimate the pressure rate of the Yb valence change as :

$$dv/dp \approx 0.005 \text{ kbar}^{-1}$$

This is in good agreement with the previous estimation ($dv/dp \approx 0.0045 \text{ kbar}^{-1}$) in [10], based on an interpolation of thermal expansion of the YbAl₂, TmAl₂ and LuAl₂ compounds.

The compressibility has been measured either directly at room temperature or calculated from the linear thermal

Fig. 3. Temperature and pressure dependence of the linear thermal expansion coefficient α of the YbInCu₄ compound

expansion measurements under fixed pressures. In the latter case, an intrinsic temperature and pressure response of the micro-strain gauges and a decrease of pressure in the cooled pressure cell were taken into account. Values of the isothermal compressibility $\kappa = -(1/V)(dV/dp) = -3(dL/L)/dp$ has been obtained as a linear fit of $V(p)/V(0)$ vs. p data. The results are presented in Fig. 4.

Fig. 4. Relative volume $V(p)/V(0)$ vs. applied pressure p at temperatures $T = 295$ K and $T = 20$ K

We have observed significantly higher value of the compressibility κ at temperature 20 K below T_V ($\kappa_{II} = 1.22 \text{ Mbar}^{-1}$) than above T_V at 295 K ($\kappa_{III} = 0.99 \text{ Mbar}^{-1}$) and the λ -shaped giant increase of the compressibility near T_V (see Fig. 5).

Fig. 5. Temperature dependence of compressibility in the vicinity of the transition temperature T_V

3. Discussion and Conclusions

Recently, the thermal expansion of the intermediate valence rare-earth compounds, with low temperature deviations, has been theoretically predicted and qualitatively described [11,12]. A well-documented phenomenological effect, that an increasing occupation of the rare earth f -shell, n_f , leads to a radial expansion of the valence orbitals (and also to a corresponding expansion of the crystal lattice) due to the enhanced screening of the nuclear charges, has been taken into account. The size of this effect is expressed by the known relation $d\ln V/dn_f \approx 0.15$ [11].

Assuming that the volume anomaly in YbInCu_4 , $\omega_v = 3\Delta L / L = 0.43\%$ at T_V , is caused by the change of the Yb atomic volume only, we have to use metallic radii of the relevant atoms to recalculate this anomaly with respect to the Yb atoms. We have estimated that the volume increase per Yb atomic volume in the YbInCu_4 compound is $\approx 1.3\%$ and the parameter $d\ln V_{Yb}/dn_f = -d\ln V_{Yb}/dv \approx 0.13$ (≈ 0.16 in the case of YbAl_2 , using the same procedure). This result surprisingly offers a possibility to describe phenomenologically the volume anomaly at the first-order valence change in YbInCu_4 as a consequence of the increasing screening of the charge of Yb nucleus. On the other hand, the smooth decrease of the volume anomaly under pressure shows the continuous increase of the Yb valence and the decreasing abrupt valence change Δv at T_V with increasing pressure.

The pressure dependence of valence v in pure Yb metal (L_{III} -absorption spectra up to 330 kbar [6]) can be fitted by expression :

$$v = 2 + 0.005 * p - 0.000007 * p^2 \quad (1)$$

where p is pressure in kbar. A rate of the continuous increase of the Yb valence in the YbInCu_4 compound under pressure is well comparable with the initial rate of the continuous pressure increase of the valence in the

pure Yb. This fact is surprising, having in mind a significant difference in the Yb-valence in the Yb and the YbInCu_4 compound under normal pressure.

The λ -shaped giant increase of the compressibility κ near T_V (see Fig.5) is compatible with a peak on the temperature dependence of specific heat c_p at T_V [1]. The independent measurements of the isothermal compressibility of the YbInCu_4 compound, κ_{II} below and κ_{III} above T_V , have shown that both values well satisfy a simple relation :

$$\kappa_{II} = \kappa_{III} + d\omega_v / dp \quad (2)$$

($d\omega_v / dp = 0.21 \text{ Mbar}^{-1}$). The compressibility κ_{III} reflects mainly compressibility of Indium and Copper, $\kappa(\text{InCu}_4) \sim 1.06 \text{ Mbar}^{-1}$ while $\kappa(\text{Yb}^{\text{metal}}) = 7.52 \text{ Mbar}^{-1}$. The high value of compressibility κ_{II} below T_V seems to be caused only by the pressure dependence of the volume anomaly that accompanies the first-order Yb-valence change in the YbInCu_4 compound. This observation supports the conclusion that the enhanced screening of the nuclear charges due to the increasing occupation of f -shell (without significant change of cohesive interatomic interactions) is the origin of the corresponding expansion of the crystal lattice.

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