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Growth of CeCoIn₅ thin films on *a*- and *r*-Al₂O₃ substrates

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Abstract

Thin films of CeCoIn₅ were deposited on *a*-plane (1120)- and *r*-plane (1102)-oriented Al₂O₃ substrates by using molecular beam epitaxy and were found to be superconductive with transition temperatures about 2 K. Their transport properties are comparable with those of the bulk material and the resistivity shows typical heavy-fermion behaviour. The growth characteristics were studied by means of x-ray diffraction and scanning tunnelling microscopy and revealed (001)-oriented growth with pronounced island formation. Based on the chemical composition of the films obtained using energy dispersive x-ray analysis, a ternary phase formation diagram was deduced.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The heavy-fermion compound CeCoIn₅ is a member of a recently discovered layered heavy-fermion family with general formula Ce_{*n*}M_{*m*}In_{3*n*+2*m*}; M = Co, Rh, Ir; *n* = 1 or 2, *m* = 0 or 1 [1]. These f-electron compounds exhibit all of the many ground states that have been observed in f-electron systems, including paramagnetism, antiferromagnetism, and exotic ambient-pressure and pressure-induced superconductivity. There exists a relationship to the high-*T*_c superconductors as well. The layered quasi-2D crystal structure of these heavy-fermion materials and that of the high-*T*_c cuprates share common features with regard to their spin-dependent electronic excitation spectrum. Early on it has been pointed out for the cuprates that such a structure in conjunction with a proximity to magnetic order is favourable for unconventional superconductivity with quasiparticle pairing mediated by magnetic correlations [2]. Such a scenario is also highly relevant for heavy-fermion materials [3].

The compound CeCoIn₅ has the highest critical temperature (*T*_c = 2.3 K) at ambient pressure of all heavy-fermion superconductors discovered to date [3]. The existence of a non-Fermi-liquid metallic state associated with quantum critical behaviour is suggested by various

experimental findings [4]. This makes CeCoIn₅ a most interesting material for understanding the relationship between antiferromagnetic correlations and superconductivity.

There is ample evidence that CeCoIn₅ is an unconventional superconductor in which the superconductive coupling is mediated not by the electron–phonon interaction but by magnetic excitations. As an example can serve the suggested d-wave character of the order parameter [5]. However, it is very difficult to get direct information of the pair-coupling mechanism, and the most promising technique in this regard is tunnelling spectroscopy. The basis for well defined planar tunnel junctions are thin films. Furthermore, other techniques to determine the order parameter symmetry, such as microwave spectroscopy, also profit from the thin film geometry. Here we report the first results on successful CeCoIn₅ thin film preparation employing molecular beam epitaxy (MBE).

2. Results and discussion

2.1. Thin film deposition

Thin films of CeCoIn₅ were deposited using MBE by co-evaporation of the constituent elements with purities of 99.9% or better from three individually controlled effusion cells. Crucible materials used were tantalum for Ce, alumina for Co, and pyrolytic boron nitride for In. The background pressure during growth ranged between 3×10^{-10} and 4×10^{-9} mbar. The system's base pressure was about 2×10^{-11} mbar. The films were grown on epitaxially polished *a*-plane and *r*-plane sapphire (α -Al₂O₃) at a typical growth rate of 0.02 nm s⁻¹. The substrate temperature during deposition was fixed at 500 °C as a consequence of some preliminary growth studies which we did with regard to the influence of the substrate temperature on CeCoIn₅ phase formation. To calibrate the material flux produced by the effusion cells, energy dispersive x-ray analyses (EDXs) of the composition of the deposited films were made, as well as individual rate calibrations of the effusion cells by means of thickness measurements for Ce, Co, and In layers employing x-ray reflectometry. All films were further characterized *ex situ* by x-ray diffraction (XRD).

2.2. Structural and compositional analysis

$\omega/2\theta$ -scans were performed on a four circle STOE x-ray diffractometer equipped with a Cu anode and a primary side carbon monochromator. The rocking curves and ϕ -scans were measured on a high-resolution Bruker MRD diffractometer with a Cu anode and a single-bounce Ge monochromator on the detector side.

CeCoIn₅ forms in the tetragonal HoCoGa₅ crystal structure with lattice constants $a = 4.62$ Å, $c = 7.56$ Å [6]. *a*- and *r*-plane sapphire has in-plane lattice constants of $a_a = 8.24$ Å, $b_a = 12.99$ Å, and $a_r = 4.76$ Å, $b_r = 15.38$ Å, respectively. From purely geometrical considerations the best lattice fit between CeCoIn₅ and sapphire would be obtained for (100)-oriented layers on *r*-plane-oriented substrates: $2c/c_r = 0.98$ and $a/a_r = 0.97$. No such growth preference was observed. Instead all $\omega/2\theta$ scans confirm a pronounced (001)-oriented growth on both substrate orientations (see figure 1). In this orientation the lattice fit along one axis is superior for growth on *r*-plane sapphire with $a/a_r = 0.97$ as compared to $a/a_a = 0.56$ for growth on *a*-plane substrates. Nevertheless, the x-ray diffraction gave no evidence for any reproducible difference with regard to the crystal quality between films grown on these two substrate orientations.

The evident peak broadening of the 00*l* reflections shown in figure 1 is caused by the mosaic structure of the CeCoIn₅ films in conjunction with the widely open detector slit during

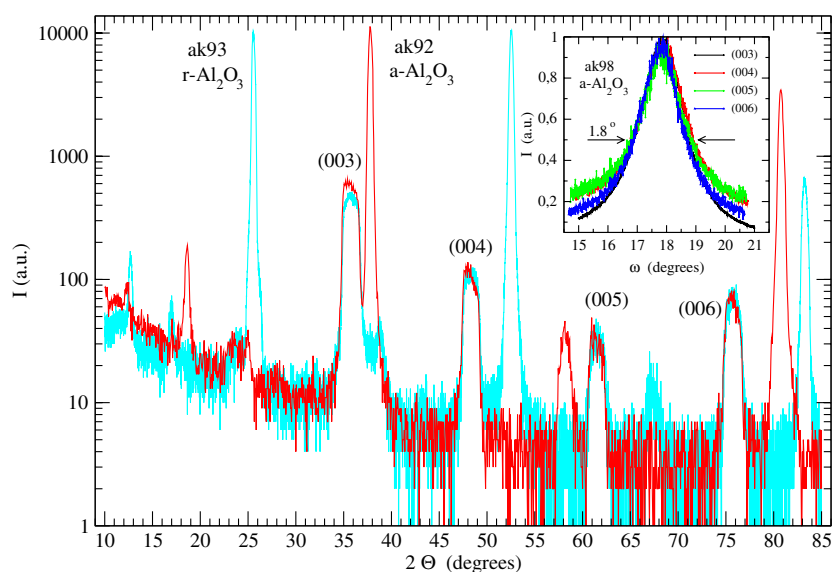


Figure 1. $\omega/2\theta$ scans of the samples *ak92* and *ak93* deposited on *a*- Al_2O_3 and *r*- Al_2O_3 substrates, respectively. In the inset the normalized rocking curves of $(00l)\text{CeCoIn}_5$ Bragg reflections are shown. The ω axes are shifted to display scans on top of each other. The large diffuse background signal is a consequence of the wide open detector slits.

the measurements. This setup was chosen to collect Bragg scattering intensity from all crystallites of the mosaic. This allowed us to determine the volume fraction of crystallized (001) -oriented CeCoIn_5 by integrating the Bragg peaks for films prepared with different element proportions. The mosaicity was further verified by measuring rocking curves of higher-order $(00l)$ reflections, which are shown in the inset of figure 1. It is evident that the rocking curves do not change with increasing reflection order. The mosaicity was determined to be 1.8° .

To identify a possible epitaxial relationship between the film and the substrate, ϕ -scans for the (200) and (400) reflection groups of CeCoIn_5 were performed for a film grown on *r*-plane sapphire in glancing incidence diffraction geometry (see figure 2). For this substrate orientation the sapphire $(11\bar{2}0)$ lattice plane is perpendicular to the sample surface and its 2θ value, 37.8° , is sufficiently close to the CeCoIn_5 (200) reflection with $2\theta = 38.9^\circ$. Film and substrate reflections could thus be observed together in one ϕ -scan for sufficiently opened detector slits. In this scan weakly pronounced maxima of intensity with fourfold symmetry correspond to the (200) Bragg reflections of CeCoIn_5 . They depict a tendency of the CeCoIn_5 structure to align its *a*-axis perpendicular to the $(11\bar{2}0)$ plane of the substrate. The ϕ -scan of the (400) reflection group of CeCoIn_5 , as shown in figure 2, further confirms this results. It can be concluded that CeCoIn_5 shows (001) -oriented textured growth with only a slight tendency to align its *a*-axis parallel to the a_r -axis of the substrate.

The observed weak epitaxial relationship occurs in conjunction with a weak adhesion of the CeCoIn_5 layers to the substrates. This results in a rough film morphology which is dominated by islands, as could be observed for some layers in optical micrographs taken in differential interference contrast, as well as in scanning tunnelling microscopy measurements in air (see figure 4). This rough microstructure was most pronounced for layers which were prepared with Ce:Co:In compositions off the ideal ratio of 1:1:5. In these cases, most probably In segregation is responsible for the weak adhesion and microstructure formation.

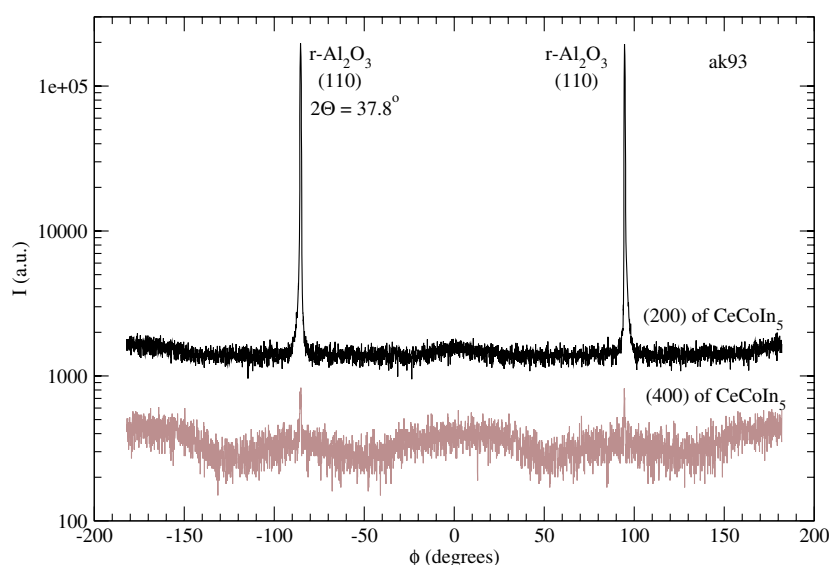


Figure 2. ϕ -scan of the CeCoIn₅ (200) reflection and (400) reflection group with the detector set at $2\theta = 38.9^\circ$ and 83.6° , respectively. The scans were made with wide open detector at the corresponding 2θ values. The 2θ value shown in the figure refers to the substrate reflection as indicated.

This conclusion can be drawn from the fact that CeCoIn₅ single-crystal growth is performed from excess In flux [3].

The chemical composition of the films was semi-quantitatively determined by EDX¹. Thin film corrections of the EDX results could not be applied because of the rough microstructure for off-stoichiometric samples. Attempts to calibrate the EDX results by means of Rutherford backscattering spectroscopy (RBS) on selected samples failed for the same reason. Nevertheless, as an important element of this work we were able to deduce a ternary phase formation diagram for (001)-oriented CeCoIn₅ thin films grown on the sapphire *r*-plane and *a*-plane by combining the EDX and x-ray diffraction results. First, the stoichiometry of ten films was determined by EDX in order to flux calibrate each effusion cell employing the Clausius–Clapeyron relationship $\ln n \propto T$ (n is the atom flux). Second, the relative volume fraction of crystalline (001)-oriented CeCoIn₅ in the films was determined by comparing the areas under the (003) reflection of CeCoIn₅ and the most prominent substrate reflection. Care was taken to properly subtract the diffuse scattering background. Exemplarily, the phase diagram for the sapphire *r*-plane appears in figure 3. From the phase diagram it is evident that a large volume fraction of phase pure (001)-oriented CeCoIn₅ can only be obtained in a very narrow homogeneity region. The MBE process is far away from the thermodynamical equilibrium, in contrast to single-crystal growth from the melt. Since the EDX measurements used to calibrate the effusion cells were made without thickness and thin films corrections, a systematic error in the film composition can arise which can account for the shift of the homogeneity region from the nominal ideal 1:1:5 composition point in the phase diagram.

¹ EDX analysis was performed with a Zeiss DSM 940a scanning electron microscope equipped with the EDAX Genesis system using the standard ZAF correction method.

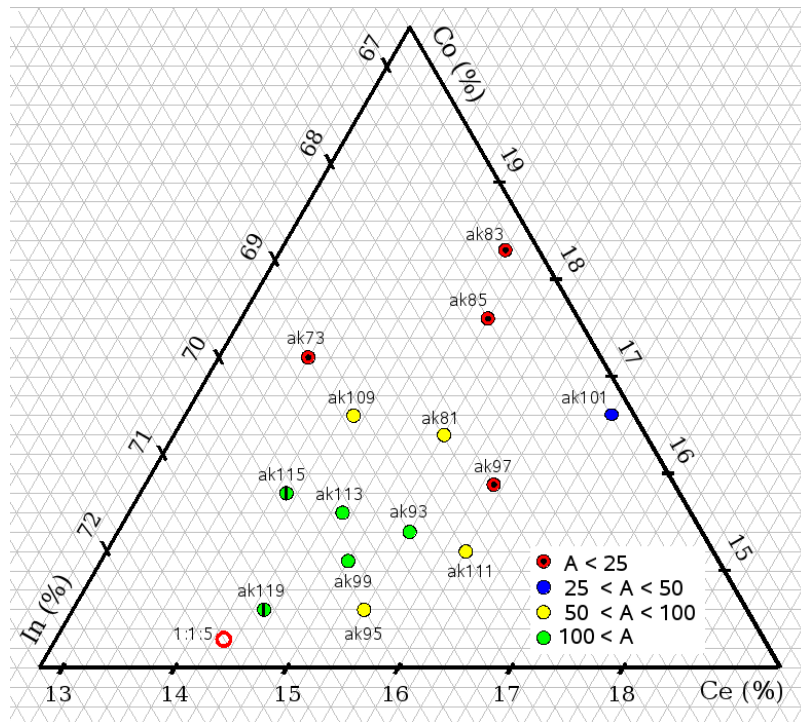


Figure 3. Ternary phase diagram of CeCoIn_5 thin films grown on *r*-plane sapphire. On the legend is given the relative amount of crystalline CeCoIn_5 defined as $A = A_{003}/A_{\text{sub}} \times 10^3$, with A_{003} being the area under the (003) CeCoIn_5 peak, and A_{sub} being the area under (01 $\bar{1}$ 2) substrate peak. Striped circles denote the presence of orientations different from (001).

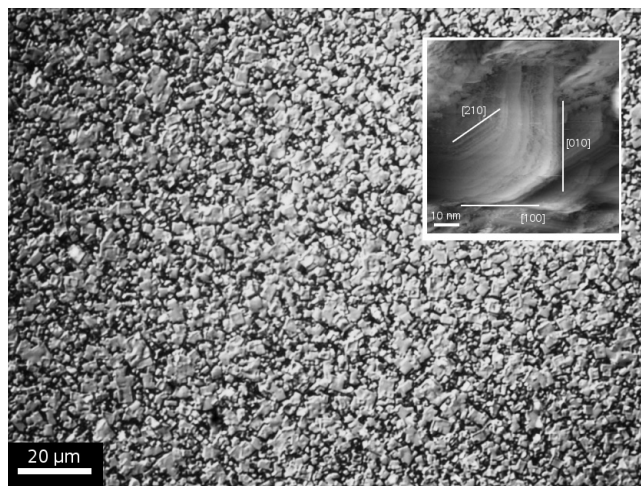


Figure 4. Optical microphotograph of the surface of sample *ak118* taken in differential interference contrast. Inset: STM surface image of sample *ak112* taken with a platinum tip in air using constant current mode with a bias voltage of 1 V and current of 1 nA. Crystal directions of the CeCoIn_5 layer are as indicated.

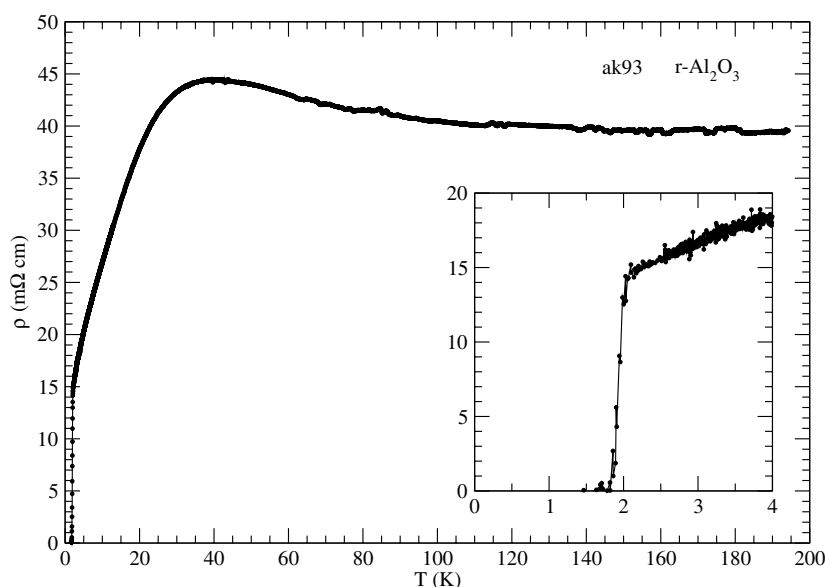


Figure 5. Temperature-dependent resistivity of CeCoIn₅ thin film grown at optimum composition. Inset: detail of the superconductive resistive transition.

2.3. Transport properties

The resistive properties of the CeCoIn₅ thin films were measured by the four-probe technique on the as-grown samples. The temperature-dependent resistance of a high-quality thin film sample is shown in figure 5. It is in excellent agreement with the results obtained on bulk CeCoIn₅ (see for example [3]). The resistance is weakly temperature dependent above approximately 35 K, where it reaches a local maximum, and shows a rapid decrease at lower temperatures. Such a behaviour is typical of heavy-fermion materials. Most importantly, in many samples a superconductive transition was observed at critical temperatures ranging between 1.6 and 2.0 K. The result obtained for the film with the largest CeCoIn₅ volume fraction appears in figure 5 with $T_C^{\text{onset}} = 2.0$ K and a transition width of 0.15 K (see inset).

The resistivity was calculated from the obtained resistance data by the van der Pauw method [7]. Typical values obtained for well-crystallized films are $45 \mu\Omega \text{ cm}$ at room temperature. These values are compatible with results which were reported for bulk CeCoIn₅. Nicklas *et al* reported for single crystals $\rho_{300} = 55 \mu\Omega \text{ cm}$ [8]; single crystals with $\rho_{300} = 38 \mu\Omega$ were prepared by Malinowski *et al* [9].

3. Conclusion

Fibre-textured (001)-oriented CeCoIn₅ thin films were grown by molecular beam epitaxy on sapphire substrates in *a*-plane and *r*-plane orientation. The film morphology tends to be rough due to a pronounced island growth mode. Only a weak epitaxial orientation relationship was observed which we attribute to a very weak layer–substrate interaction. The homogeneity region for the phase-pure formation of (001)-oriented layers is limited to a few per cent. The temperature-dependent resistivity of the layers is in full agreement with typical results obtained for bulk CeCoIn₅. In particular, superconductivity was routinely observed in the layers, with critical temperatures up to 2.0 K.

Further research will now focus on optimizing the phase formation process by systematically varying the substrate temperature. Most importantly, alternative substrate materials and orientations will be elucidated for obtaining epitaxial growth. As a prerequisite for the suggested tunnelling diode preparation, the film morphology has to be improved towards a smoother surface.

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