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Structural stability of LaCu_2 and YCu_2 studied by high-pressure x-ray diffraction and *ab initio* total energy calculations

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Abstract. LaCu_2 is the only compound among the RCu_2 series (R from La to Lu, and Y) which crystallizes in the hexagonal AlB_2 -type structure, whereas the other compounds show the orthorhombic CeCu_2 -type structure. In agreement with *ab initio* calculations our high-pressure x-ray diffraction experiments show that LaCu_2 transforms at relatively low pressures to the CeCu_2 -type structure, which can be regarded as a low-symmetry variant of the AlB_2 -type structure.

To investigate the stability of the CeCu_2 -type structure we performed high-pressure x-ray diffraction experiments on YCu_2 using argon as the pressure transmitting medium. These experiments showed in contrast to an earlier study that the CeCu_2 structure is stable at least up to the highest attained pressure of 35 GPa. The tendency for amorphization at pressures above 10 GPa, as observed in the earlier study, was probably due to the non-hydrostatic conditions of the pressure transmitting medium, showing that the CeCu_2 -type compounds are very sensitive to non-hydrostatic compression. A transition to the MgCu_2 -type structure (cubic Laves phase) at about 28 GPa, as predicted by the *ab initio* calculations, has not been observed.

1. Introduction

Among the RCu_2 series (R = Y, La, Ce–Lu) only LaCu_2 does not show the orthorhombic CeCu_2 -type structure (space group *Imma*) at ambient pressure and temperature. In contrast to the other compounds it crystallizes in the hexagonal AlB_2 -type structure (*P6/mmm*). However, a comparison of these two structure types shows that they are closely related, i.e. the CeCu_2 -type structure is a low-symmetry variant of the AlB_2 -type structure. This relation is for instance important for an axis conversion effect discovered in several orthorhombic RCu_2 compounds [1, 2]: the magnetic easy axis can be rotated by the application of a high magnetic field along the hard axis, and this conversion process is connected with a transition from orthorhombic to hexagonal symmetry.

The first subject of the present work was to perform high-pressure x-ray diffraction experiments as well as *ab initio* total energy calculations on LaCu_2 , in order to study the stability of the AlB_2 type with respect to a possible pressure-induced transition to the CeCu_2 -type structure. Such a transition seems at least plausible, since La is the largest atom among all R atoms, i.e. a smaller volume seems to favour the formation of the CeCu_2 -type.

The second subject of the paper concerns YCu_2 , which shows the CeCu_2 -type structure at ambient conditions and therefore can be regarded as a representative of the other RCu_2 compounds. An earlier study [3], also using high-pressure x-ray diffraction and *ab initio* calculations, showed a good agreement between the calculated and measured pressure dependence of the orthorhombic lattice parameters up to about 10 GPa. Above this pressure a very strong irreversible line broadening of the x-ray lines was observed. One possible reason for this strong line broadening, which appeared to indicate the onset of amorphization, could be a kinetically frustrated phase transition to the MgCu_2 -type structure (cubic Laves phase), which has been predicted by the *ab initio* calculations to take place at about 28 GPa. The second reason could be a very high sensitivity of the CeCu_2 -type compounds to non-hydrostatic compression. In order to clarify these questions, we present new high-pressure x-ray diffraction experiments on YCu_2 using argon as the pressure transmitting medium, which remains more hydrostatic at high pressures than other media such as methanol–ethanol mixtures or oil.

2. Experimental and theoretical background

2.1. Preparation of the samples

Polycrystalline samples of LaCu_2 and YCu_2 were prepared by arc-melting appropriate portions of the pure elements under argon atmosphere. The occurrence of a Cu-rich phase found in preliminary test samples of LaCu_2 was connected with a small amount of oxygen in the starting La and could be prevented by a slight concentration shift in comparison to the stoichiometric composition. The phase purity of the samples was checked by x-ray-diffraction measurements on powdered sample pieces. The metallographic inspection showed a large-grained microstructure for both samples, and in the case of LaCu_2 also traces (<1%) of La_2O_3 .

2.2. High-pressure x-ray powder diffraction experiments

The experimental studies were performed at the ID 30 beamline of the European Synchrotron Radiation Facility (ESRF, Grenoble, France), using a monochromatic x-ray beam with a wavelength of 0.3066 Å. The x-ray patterns were obtained by integrating over the diffraction rings of the FASTSCAN image-plate detector system [4] using the Fit2D program [5]. The measurements were made at room temperature on powdered samples using a Syassen–Holzapfel type diamond anvil cell [6]. Microsamples of the material and a ruby splinter for pressure determination were loaded into a 0.2 mm hole drilled into an annealed (800 °C for 3 hours) and pre-indented Inconel X750 gasket. The beam size at the sample was about $0.1 \times 0.1 \text{ mm}^2$. Silicone oil and argon (cryogenic loading) were used as the pressure transmitting media.

2.3. *Ab initio* total-energy calculations

Ab initio calculations of the total energy were performed using the Vienna *ab initio* simulation package VASP [7, 8], which allows us to minimize the total energy with respect to the volume and shape of the unit cell and to the positions of the atoms within the cell, with no other

restrictions than those imposed by space-group symmetry. For details of the calculations we refer to our earlier study [3] and references therein. In the case of LaCu_2 the so-called projector augmented-wave (PAW) method was used instead of the ultrasoft pseudopotential method, which cannot be used for the lanthanides (La, Ce etc). A description of the PAW method and a way to implement it in existing plane-wave codes like VASP is given in [9] and [10]. For La not only the three electrons exceeding the [Xe]-configuration were treated as valence electrons, but also the 5s and the 5p electrons. Similarly, for Y not only the three electrons exceeding the [Kr]-configuration were treated as valence electrons, but also the 4p electrons. As in the previous work [3] we used generalized gradient corrections to the local density functional. Convergence of the results with respect to the k -point mesh for BZ integrations, the fast-Fourier-transform meshes used for the representation of the wavefunctions, charge densities and potentials, and with respect to the cut-off energy of the plane-wave basis set was carefully tested. Furthermore it is possible to perform the total energy calculations for both the CeCu_2 type and the AlB_2 type using the same unit cell (since the AlB_2 -type structure can be obtained from the CeCu_2 -type structure by only changing some structural parameters which are not fixed by the space-group symmetry of the CeCu_2 type—see section 3.1). This was done in order to omit possible small errors in the energy difference of the two structures arising from choosing different unit cells for the calculations.

3. Results and discussion

3.1. Relationship between the CeCu_2 -type and AlB_2 -type crystal structures

The CeCu_2 -type structure is described within the orthorhombic space group $Imma$ with the R atoms on the 4e sites and the Cu atoms on the 8h sites. The primitive unit cell of the body-centred orthorhombic lattice contains six atoms (2 R, 4 Cu) and there are three atomic position parameters which are not fixed by the space group symmetry: z_R , y_{Cu} and z_{Cu} . In the case of YCu_2 , as an example, these parameters are $z_R = 0.544 \pm 0.002$, $y_{Cu} = 0.050 \pm 0.002$ and $z_{Cu} = 0.162 \pm 0.002$, and the lattice parameters are $a = 4.301 \pm 0.001 \text{ \AA}$, $b = 6.874 \pm 0.003 \text{ \AA}$ and $c = 7.297 \pm 0.001 \text{ \AA}$ at ambient pressure and temperature (see for instance [3, 11]). If the ratio of the lattice parameters c/a ($=1.697$) were $\sqrt{3}$ ($=1.732$) and if $z_R = 1/2$ (instead of 0.544), $y_{Cu} = 0$ (instead of 0.050) and $z_{Cu} = 1/6$ (instead of 0.162), then we would obtain the AlB_2 -type structure. This structure, which can be described with the space group $P6/mmm$ (Y on the 1a sites and Cu on the 2d sites), contains three atoms (2 R, 1 Cu) in the primitive unit cell with all atomic position parameters fixed by symmetry. This means that the two structures are closely related and the CeCu_2 type is only a low-symmetry variant of the AlB_2 -type structure. The upper part of figure 1 shows the hexagonal cell of the AlB_2 -type structure (R atoms: black, Cu atoms: grey), visualizing the high symmetry of this structure type (simple hexagonal Cu planes between close-packed hexagonal R planes). The lower part of figure 1 shows the AlB_2 -type structure in the orthorhombic description corresponding to the CeCu_2 -type structure (with $a_{ortho} = a_{hex}$, $b_{ortho} = 2c_{hex}$ and $c_{ortho} = \sqrt{3}a_{hex}$) and the CeCu_2 -type structure itself. From this comparison we see that the CeCu_2 type is obtained from the AlB_2 -type structure by shifting and distorting the R planes in the direction of c_{ortho} (since z_R differs by 0.044 from 1/2), and by a zig-zag bending of the Cu planes in the b_{ortho} direction (since y_{Cu} differs by 0.050 from 0). The shifting of the Cu atoms in the c_{ortho} direction is negligible: it is about ten times smaller than the other atom shifts (since z_{Cu} differs only by 0.005 from 1/6—this difference is not much larger than the experimental error).

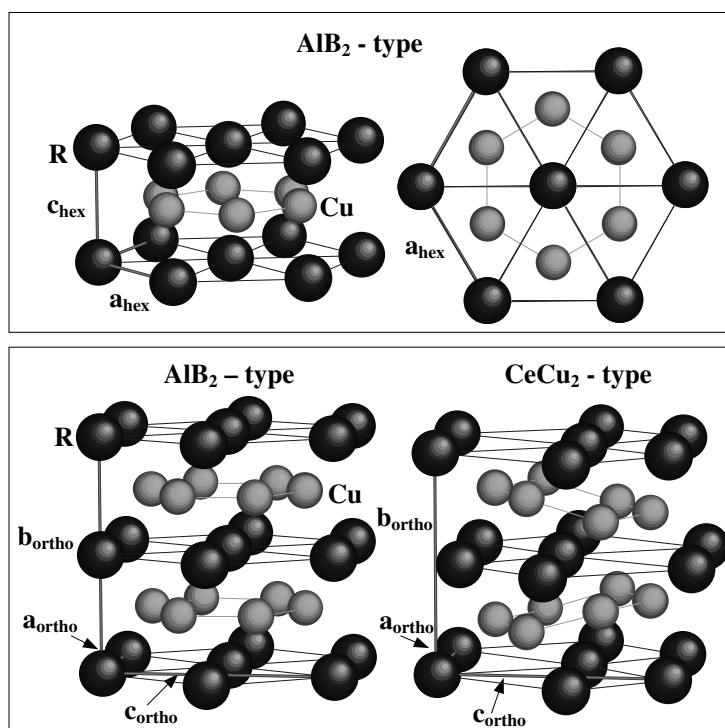


Figure 1. Upper part: hexagonal cell of the AlB₂-type structure. Lower part: comparison with the orthorhombic CeCu₂-type structure.

3.2. Pressure-induced structural phase transition in LaCu₂ (AlB₂ type → CeCu₂ type)

In figure 2 the calculated total energy as a function of the volume is shown for both the AlB₂- and the CeCu₂-type structures. The reason for the missing points for the CeCu₂-type structure at higher volumes is that the structural parameters, which are not fixed by the space group symmetry of *Imma*, relax to the special values mentioned in the previous section ($z_R \rightarrow 1/2$, $y_{\text{Cu}} \rightarrow 0$, $z_{\text{Cu}} \rightarrow 1/6$, $c_{\text{ortho}}/a_{\text{ortho}} \rightarrow \sqrt{3}$), i.e. the CeCu₂ type relaxes to the AlB₂-type structure during the minimization of the total energy with respect to the structural parameters. However, it is clear that without external pressure the AlB₂ type is the stable structure and that there is a crossing of the two curves indicating a pressure-induced phase transition. The slope of the common tangent to the two curves is $\Delta E/\Delta V = 3.9$ GPa, i.e. the transition should take place at about this pressure.

As shown in figure 3, this predicted AlB₂ → CeCu₂ transition is also found by our high-pressure x-ray diffraction experiments. The figure shows the integrated x-ray patterns at pressures up to 5.6 GPa and at the highest attained pressure of 21.2 GPa. The pattern at 0 GPa contains only the x-ray lines of the AlB₂-type structure, but already at 1.6 GPa additional lines appear, which can be identified as lines of the CeCu₂-type structure, and at 3.9 GPa the transition is completed, i.e. the transition occurs already at a pressure roughly 2 GPa lower than expected from the *ab initio* calculations. Then there is no further change of the structure up to 21.2 GPa. Due to the non-hydrostatic conditions above about 5–7 GPa, caused by the freezing of the pressure transmitting medium silicone oil (see for instance [12]), there is an increasing line broadening, which is maintained after pressure release. This line broadening makes it

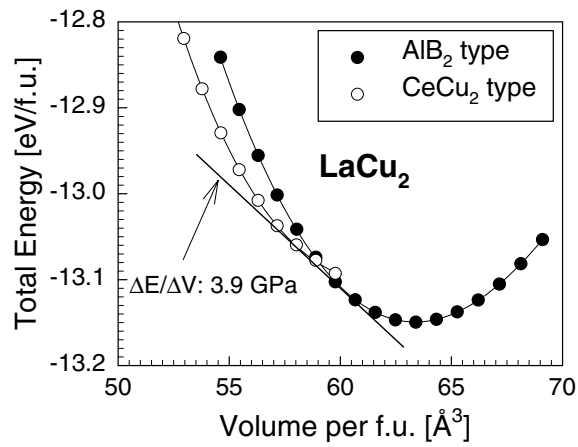


Figure 2. *Ab initio* total energy as a function of the volume for LaCu_2 in the AlB_2 -type and CeCu_2 -type structures.

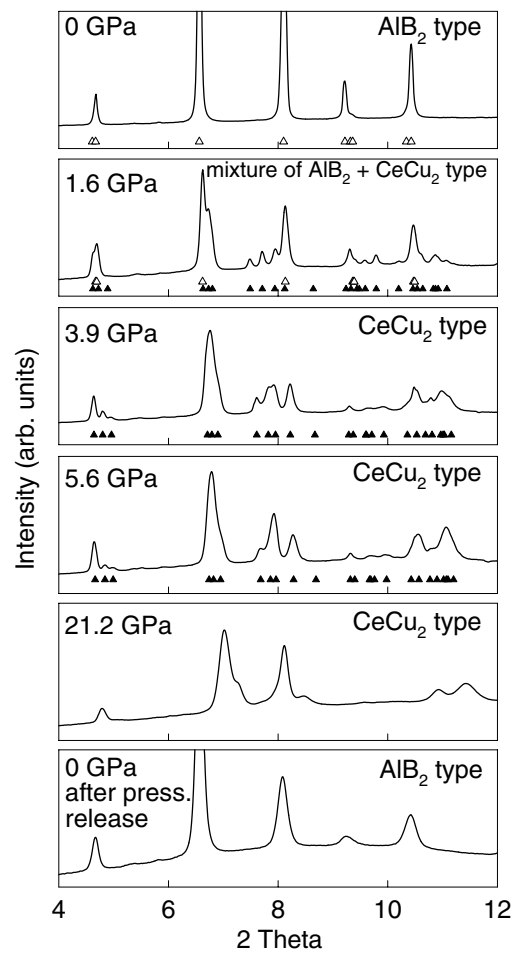


Figure 3. X-ray patterns of LaCu_2 at different pressures. The open and full triangles indicate the positions of the x-ray lines of the AlB_2 -type and CeCu_2 -type structures, respectively.

Table 1. Experimental values of the lattice parameters of LaCu₂ at different pressures at ambient temperature for the AlB₂-type and the CeCu₂-type phases.

	AlB ₂ -type phase		CeCu ₂ -type phase		
	a_{hex}	c_{hex}	a_{ortho}	b_{ortho}	c_{ortho}
0 GPa	4.341 ± 0.002 Å	3.815 ± 0.002 Å	—	—	—
1.6 GPa	4.325 ± 0.004 Å	3.759 ± 0.006 Å	4.428 ± 0.004 Å	7.187 ± 0.012 Å	7.450 ± 0.008 Å
3.9 GPa	—	—	4.441 ± 0.002 Å	7.107 ± 0.015 Å	7.323 ± 0.005 Å
5.6 GPa	—	—	4.434 ± 0.003 Å	7.057 ± 0.009 Å	7.260 ± 0.009 Å
0 GPa ↓	4.351 ± 0.003 Å	3.807 ± 0.003 Å	—	—	—

very difficult to determine precisely the orthorhombic lattice parameters for our x-ray patterns above 5.6 GPa. However, the interesting pressure range lies between 0 and 5 GPa, which was in fact the reason for choosing silicone oil, which is easier to handle at lower pressures than other pressure transmitting media.

Figure 4 shows the experimentally determined lattice parameters and the relative unit cell volume $V(P)/V(P = 0 \text{ GPa})$ as a function of the applied pressure P together with the values of the *ab initio* calculations (crosses). The only larger discrepancy concerns the value of the lattice parameter c_{hex} of the AlB₂-type structure at 0 GPa and 1.6 GPa. This parameter is overestimated by the calculations by 1.4%, which is also the main reason for the differences in the $V(P)/V(P = 0 \text{ GPa})$ curves at higher pressures (since $V(P = 0 \text{ GPa})$ is overestimated by the calculation). It is interesting to note that it is just this lattice parameter which is mostly affected by the phase transition, i.e. the value $2c_{hex}$, which corresponds to the orthorhombic b_{ortho} , shrinks by 4.4% at the transition (taken from the experimental values at 1.6 GPa). This means that the nature of the AlB₂ → CeCu₂ transition is mainly a decrease of the distance between the hexagonal La and Cu planes, which is slightly overestimated by the *ab initio* calculations. The distortion of the hexagonal planes, which is reflected in the pressure dependence of the other lattice parameters a_{hex} , a_{ortho} and c_{ortho} , is in good agreement with the calculations. There is a pronounced elongation of the hexagonal planes in the a_{ortho} direction by 2.3% and a slight shrinking in the c_{ortho} direction by 0.6%, but the elongation in the a_{ortho} direction is strongly overcompensated by the above discussed shrinking in the b_{ortho} direction, leading to a volume decrease of 2.7% at the transition. Because of the volume jump an analysis of the compressibility by fitting an equation of state function is not possible. The slope of the $V(P)/V(P = 0 \text{ GPa})$ curve of the AlB₂ phase between 0 GPa and 1.6 GPa corresponds to a bulk modulus K_0 of about 73 GPa.

After pressure release from 21.2 GPa the sample showed again the AlB₂-type structure (figure 3) with slightly different lattice parameters than before applying the pressure (the differences lie almost within the size of the symbols in figure 4, see table 1). This means that the reversibility of the transition is not affected by the strains, which are reflected in the strong line broadening at pressures above 5–7 GPa and which are maintained after pressure release.

For completeness the experimental values of the lattice parameters for both phases are also summarized in table 1.

In connection with the volume decrease of 2.7% at the transition it is very instructive to make a comparison of the volumes at ambient conditions with the neighbouring RCu₂ compounds, which all crystallize in the CeCu₂-type structure. As shown in figure 5, there is the expected and well known Z -dependence of the volumes for the trivalent rare earth atoms (lanthanide contraction), whereas the volume of the AlB₂-type compound LaCu₂ is much too large (by 5.0%), i.e. the volume of a hypothetical LaCu₂ with the CeCu₂-type structure

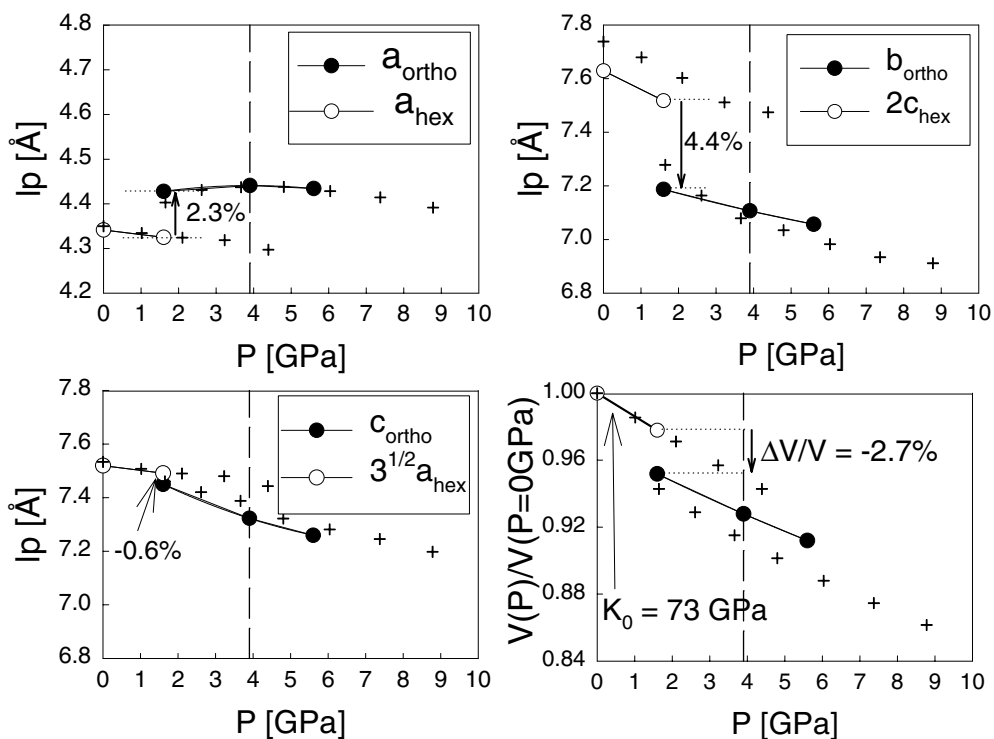


Figure 4. Pressure dependence of the lattice parameters (lps) and the unit cell volume for the AlB_2 -type and CeCu_2 -type phases of LaCu_2 . The circles denote the experimental values (open: AlB_2 , full: CeCu_2) and the crosses indicate the results of the *ab initio* calculations. The vertical dashed line shows the calculated transition pressure. The chosen scaling for the lattice parameters allows a comparison of the relative changes.

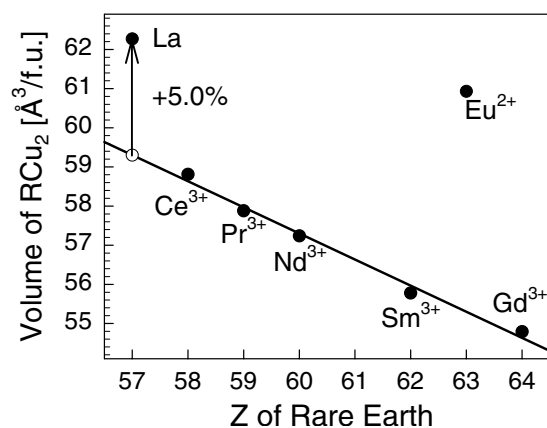


Figure 5. Comparison of the volumes at ambient conditions between LaCu_2 and the neighbouring RCu_2 compounds.

should have a much smaller volume. This argument alone is a good reason for expecting the observed pressure-induced phase transition to the CeCu_2 -type structure accompanied by a volume decrease in LaCu_2 .

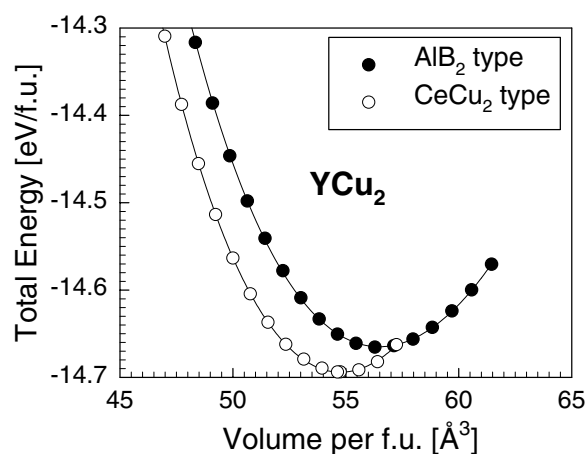


Figure 6. *Ab initio* total energy as a function of the volume for YCu_2 in the AlB_2 -type and CeCu_2 -type structures.

3.3. Stability of the CeCu_2 -type structure of YCu_2

Figure 6 shows the calculated total energy as a function of the volume for both the AlB_2 - and the CeCu_2 -type structures in the case of YCu_2 . In agreement with the experiment the CeCu_2 -type structure is already energetically favourable at ambient pressure. As can be seen from the figure the equilibrium volume of the AlB_2 -type structure would be about 3% larger than that of the CeCu_2 -type structure. This means that the AlB_2 -type structure is intimately connected with a larger volume—not only in the case of LaCu_2 .

As already mentioned in the introduction, we observed in an earlier study of YCu_2 (and also of NdCu_2 and GdCu_2) a very strong line broadening of the x-ray lines of the CeCu_2 -type structure at pressures above about 10 GPa [3]. The pressure-transmitting media used (4:1 methanol–ethanol mixture and silicone oil) lose their hydrostatic properties already at relatively low pressures: the freezing point is about 5–7 GPa for the oil and 10–12 GPa for the methanol–ethanol mixture (but the hydrostatic limit could even be lower—see for instance [12]). However, the line broadening was so strong (appearing to indicate the onset of an amorphization) that it was not attributed to the non-hydrostatic pressure, but to a kinetically frustrated structural phase transition to the MgCu_2 -type structure, which was predicted by the *ab initio* calculations to take place at 28 GPa [3]. Kinetically frustrated means that the predicted transition does not take place because the kinetic energy of the atoms at ambient temperature is not high enough to overcome the energy barrier between the two structures, although the MgCu_2 -type structure becomes energetically favourable at high pressures. This assumption of a kinetically frustrated phase transition is plausible, since there exists no simple transformation path between the CeCu_2 -type and the MgCu_2 -type structure.

Considering these points we made two improvements for our new experiments on YCu_2 :

- (i) we used argon as pressure transmitting medium, in order to keep hydrostatic or quasi-hydrostatic conditions up to higher pressures, and
- (ii) in order to relax strains and to increase the kinetic energy of the atoms, we heated the sample at the highest attained pressure of 35.4 GPa by putting the whole cell for several hours in an oven at 220 °C, as well as by laser-heating the sample up to glowing for several minutes.

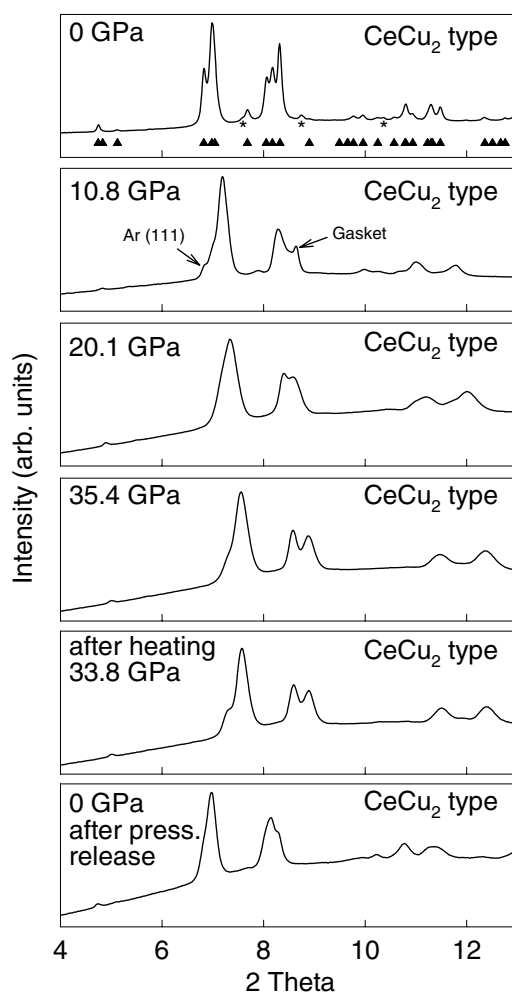


Figure 7. X-ray patterns of YCu_2 at different pressures. The full triangles in the first pattern indicate the positions of the x-ray lines of the CeCu_2 -type structure; the asterisks indicate small impurity lines.

The results of these experiments are shown in figure 7. Except for some small impurities all the lines at 0 GPa can be indexed assuming the CeCu_2 -type structure with lattice parameters $a = 4.304 \pm 0.001 \text{ \AA}$, $b = 6.866 \pm 0.003 \text{ \AA}$, $c = 7.280 \pm 0.004 \text{ \AA}$. But as can be seen there is already at 10.8 GPa a strong line broadening, although the pressure transmitting medium (argon) has much better hydrostatic conditions at this pressure than a methanol-ethanol mixture or oil, which were used in the earlier study [3]. This line broadening makes an accurate determination of the orthorhombic lattice parameters impossible. The extent of the line broadening also becomes visible by comparison with the strongest x-ray line of the gasket, which was accidentally hit by the x-ray beam at 10.8 GPa. Furthermore the predicted structural phase transition to the cubic MgCu_2 -type structure is not observed up to 35.4 GPa and the only effect obtained by heating the sample (besides a small pressure decrease to 33.8 GPa) is a slight narrowing of the diffraction lines. This observed disagreement between the experiments and the *ab initio* calculations is probably due to an extremely high sensitivity of the crystal

structure to non-hydrostatic compression, which is together with a possible kinetic frustration the main reason for the suppression of the transition to the energetically favourable MgCu₂-type structure. This conclusion is supported by the fact that the agreement between the experiment and the *ab initio* calculation is very good in the pressure range below 10 GPa, as can be seen by a comparison of the calculated and measured pressure dependence of the lattice parameters [3]. The strong influence of the non-hydrostatic pressure on the structural stability at higher pressures is not taken into account by the *ab initio* calculations, which assume an absolutely hydrostatic compression.

Acknowledgments

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