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# Simultaneous determination of the electronic and chemical structures in $\text{CeNi}_x\text{Cu}_{5-x}$ at high pressures

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## Abstract

Combined x-ray diffraction and x-ray absorption results are presented on the substitutional Ce valence transition in  $\text{CeNi}_x\text{Cu}_{5-x}$  as a function of applied external pressure. No significant influence of pressure on the valence in the near-transition region of  $x$  is found in the crystal structure or in the Ce K-edge position. This result is discussed in the context of valence instabilities in intermetallic Ce compounds.

## 1. Introduction

Valence fluctuations in rare earth intermetallics result in interesting features, in particular the formation of a non-magnetic ground state and strong coupling between the valence fluctuations and the lattice. Ce intermetallics have attracted special attention because Ce can fluctuate between the non-magnetic  $4f^0$  and the magnetic  $4f^1$  configurations. In many valence-fluctuating systems, the valence fluctuations, and hence the corresponding electronic and magnetic properties, can be influenced by substitution and/or doping. General information on valence fluctuations in solids can be found in e.g. [1]. In addition, the physical properties of these materials are unusually strongly influenced by external parameters such as temperature and pressure.

For Ce, the change between the  $4f^0$  and  $4f^1$  ground state is associated with a change in the ionic radius, and therefore for Ce incorporated in a crystal structure a strong variation in unit cell volume is expected. From the structural point of view, pressure is expected to exert a much stronger influence on the electronic structure than is temperature. Pressure-dependent collapses in unit cell volume have been observed for the  $\alpha$ - $\gamma$  transition in Ce [2] as well as for a phase transition in CeNi [3]. The microscopic origin of these phase transitions is still controversial ( $\alpha$ - $\gamma$  Ce) [2] or of unknown nature (CeNi) [3]. The important question to study

is the relationship between the effects of chemical pressure produced by substitution and real external pressure on the electronic structure and crystal lattice parameters.

An ideal candidate for the study of a possible electronic phase transition as a function of pressure would be a material with a  $4f^1$  ground state which can be tuned close to an electronic instability. Therefore, a Ce-based material which can be transformed by substitution from the  $4f^1$  to the  $4f^0$  ground state configuration would be appropriate, with a composition in the vicinity of a phase transition.

$\text{CeNi}_x\text{Cu}_{5-x}$  crystallizes in the  $P6/mmm$  symmetry with  $a = 4.88 \text{ \AA}$  and  $c = 4.003 \text{ \AA}$  at ambient temperatures, and with Ce occupying the (1a) site. For a continuous solid solution  $\text{CeNi}_x\text{Cu}_{5-x}$ , the Ni and Cu ions are randomly occupying the (2c) and (3g) sites. It is well known that upon substitution of Cu by Ni, the system undergoes a phase transition, from a Kondo system for  $x = 0$ , with Ce accurately described as a  $4f^1$  configuration hybridized with the conduction electrons, to a non-magnetic  $4f^0$  configuration ( $x$  approaches 5), which can be viewed as delocalized  $4f$  states.

Here we present results on the pressure dependence of the electronic and crystallographic structure of  $\text{CeNi}_x\text{Cu}_{5-x}$ . Simultaneous x-ray absorption and x-ray diffraction experiments have been performed in the vicinity of the Ce K-edge, indicating that pressures up to 40 GPa give only a weak disturbance to the electronic structure of Ce, despite a large change in the unit cell volume.

## 2. Experiments

The samples were prepared in the Baikov Institute of Metallurgy, Moscow, by arc melting in a furnace with a non-consumable tungsten electrode in purified helium at a pressure of 40 kPa. The starting materials were 99% pure rare earth metals and 99.99% pure nickel and copper. After preparation samples were annealed at  $800 \text{ }^\circ\text{C}$  for approximately 24 h. Characterization by x-ray diffraction on the laboratory diffractometer at the Kurchatov Institute, Moscow, showed no evidence of impurity phases.

The high-pressure experiments were performed at ID9 at the European Synchrotron Radiation Facility, Grenoble (ESRF). A diamond anvil cell with an aperture of  $125 \text{ }\mu\text{m}$  was used, with liquid  $\text{N}_2$  as a pressure medium. A polished and dynamically bent Si(311) crystal served as a dispersive monochromator giving an energy resolution of approximately 2 eV. A focus of  $15 \text{ }\mu\text{m}$  was obtained, with a band pass of 3% (1.2 keV) at the 40 keV Ce K-edge. A CCD camera provided position-sensitive intensities, which were then transformed to photon energy. By introducing a slit in front of the diamond anvil cell, the bandwidth was reduced to  $10^{-3}$ , allowing a powder diffraction data set to be collected at each pressure in addition to the dispersive EXAFS. A high-resolution ( $100 \times 100 \text{ }\mu\text{m}$  pixel size) image plate of size ( $350 \text{ mm} \times 430 \text{ mm}$ ) was used as the detector. Additional details of the experimental set-up will be published elsewhere [4]. Absorption measurements on a Ce standard at ambient pressure were performed at the ID15 high-energy beamline at the ESRF.

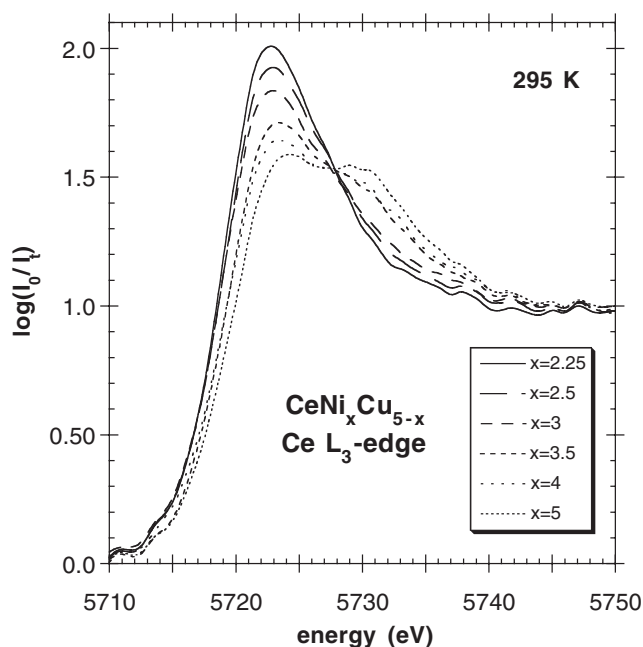
The x-ray absorption measurements at the Ce  $L_3$ -edge were performed at the dispersive EXAFS beamline ID24 at the ESRF. The sample was ground to a fine powder and mixed with weakly absorbing boron nitride. Since the incoming ID24 beam was inhomogeneous due to the phase contrast produced by imperfections of the optics, sample inhomogeneities significantly distorted the observed absorption spectra. In order to improve the quality of the data, the sample underwent a pseudorandom motion, and approximately 100 spectra were averaged. This procedure resulted in data of reasonable quality.

### 3. Results and discussion

Figure 1 shows the L<sub>3</sub>-edge spectra for CeNi<sub>x</sub>Cu<sub>5-x</sub> for different  $x$ . For  $x \leq 2.25$ , the Ce L<sub>3</sub>-edge exhibits a single resonance, representing a Ce valence close to trivalent. Upon increasing  $x$ , an additional component at approximately 8 eV above the resonance appears, which is reminiscent of a contribution of the 4f<sup>0</sup> configuration. Note that these results are comparable with those in [5]. Therefore, a value of  $x$  close to the critical concentration for the phase transition ( $x = 3.25$ ) is ideal for the study of the effect of pressure on the electronic and crystal structure. Figure 2 shows the raw data for a powder diffraction pattern of CeNi<sub>3</sub>Cu<sub>2</sub> taken with an image plate at 8 GPa. The data were corrected for the zero shift of the centre and then integrated along the powder diffraction rings to obtain the one-dimensional data set shown in figure 3. Energy calibration and the conversion from pixels to scattering angles  $2\theta$  was performed by using an Si standard data set. The diffraction patterns were then analysed using the Fullprof Rietveld refinement code [6]. Since the metal ions are located at special positions, the only relevant structural fitting parameters are the lattice constants  $a$  and  $c$  of the hexagonal unit cell, which are presented in figure 4 as a function of pressure. As an inset, the unit cell volume and the  $c/a$  ratio are shown as a function of pressure. There is no clear anomaly visible, neither in the lattice constants nor in the unit cell volume, between 3 and 40 GPa pressure at ambient temperature. This is in contrast with the unconventional change with  $x$  observed in the lattice constants and unit cell volume [5]. The ratio of  $a/c$  decreases slightly for increasing pressures, distorting the structure further from cubic ( $a/c = \sqrt{8/3} = 1.633$ ). For close packing of spherical ions,  $a$  is equally influenced by the ionic radii of the metal and rare earth ions, and  $c$  is dominated by the radii of the transition metal ions. Therefore, the ionic radii of all three constituent ions significantly decrease as a function of pressure. Note that the lattice parameters corresponding to CeNi<sub>5</sub> are reached at approximately 6 GPa, as shown by a line in figure 4.

Figure 5 shows the EXAFS spectra of CeNi<sub>3</sub>Cu<sub>2</sub> and CeNi<sub>5</sub> at the Ce K-edge taken in a regular step mode at ID15 of the ESRF. A clear edge shift is visible between these two data sets and from an edge fit to an arctan function a value of  $3.5 \pm 0.4$  eV is obtained. Figure 6 shows the dispersive EXAFS spectra of CeNi<sub>3</sub>Cu<sub>2</sub> at the Ce K-edge at a pressure of 20 GPa. The inset shows an enlarged region for the data taken at 1.3 and 40 GPa, visualizing only a small energy shift at the Ce K-edge due to the applied pressure. The background modulations above and below the edge are due to inhomogeneities in the polycrystalline sample. Phase contrast of the incoming beam is caused by the surface imperfections of the optical components leading to a horizontally inhomogeneous intensity distribution. This distribution is further distorted by phase contrast from imperfections in the sample. The result is an incomplete cancellation in the normalization process and hence a slight distortion of the absorption spectra.

It has been shown in the past that the rare earth K-edges (dipole  $s \rightarrow p$  transition) do not exhibit a white line feature [7] for metals, in contrast to oxides [8, 9]. The difference in the energy position of the Ce K-edge for CeO<sub>2</sub> and CeNi<sub>5</sub>, both with similar valences of 3.35 and 3.46 respectively, is a relatively large 7.5 eV. In addition, for CeO<sub>2</sub>, there are EXAFS modulations evident at the Ce K-edge (see figure 7), whereas only a step is observed for CeNi<sub>5</sub> (figure 5). Moreover, the broadening of the Ce K-edge is distinctly smaller for CeO<sub>2</sub> than for CeNi<sub>5</sub>. All these differences are based on the different electronic structure for nominally 4+ Ce in CeO<sub>2</sub> and CeNi<sub>5</sub>. It may be argued that in the metallic CeNi<sub>5</sub> there are conduction electrons with p character which can rapidly fill the core hole. This is in contrast to the insulating CeO<sub>2</sub>, which has a gap at the Fermi surface and the states with p character are either completely filled or not occupied. Therefore a bound p electron has to fill the s core hole, which is a slower process than the one in CeNi<sub>5</sub> and therefore leads to the smaller edge

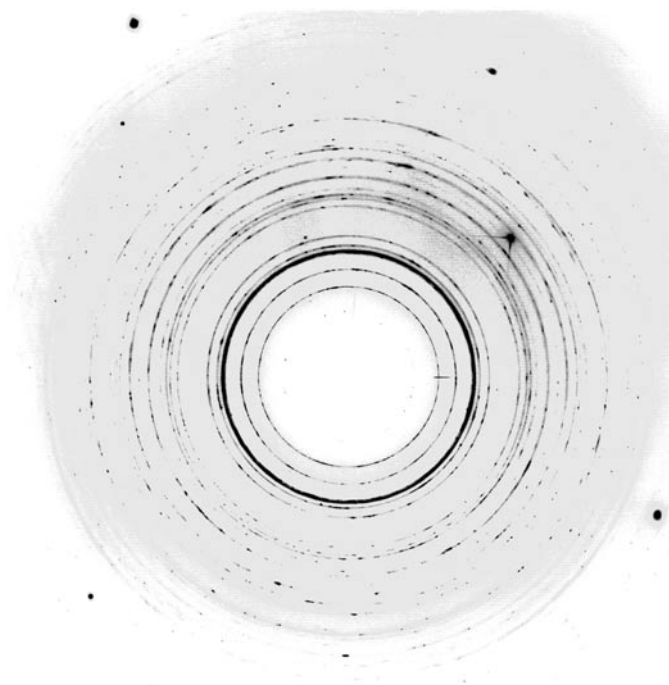


**Figure 1.** Normalized x-ray absorption spectra in transmission mode of  $\text{CeNi}_x\text{Cu}_{5-x}$ , taken at ID24 at ambient pressure and temperature in the vicinity of the  $L_3$ -edge of Ce.

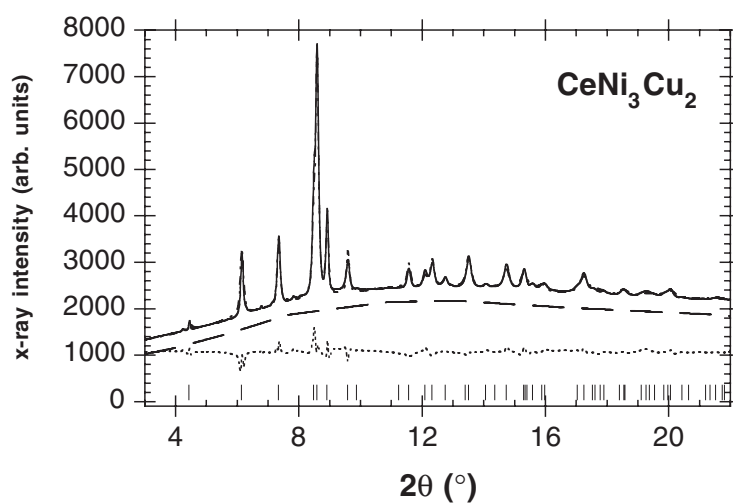
broadening. The unoccupied p density of states give rise to the white line feature in the oxide. Therefore, the pressure-induced edge shift cannot be related to the edge of Ce in  $\text{CeO}_2$  but only to that of  $\text{CeNi}_5$ .

The pressure-induced shift in the Ce K-edge is shown in figure 8 for  $\text{CeNi}_3\text{Cu}_2$  and  $\text{CeNi}_{3.5}\text{Cu}_{1.5}$ . A linear fit to the energy dependence of the edge shows that for increasing pressures, the edge energies increase slightly with a slope of  $0.015 \text{ eV GPa}^{-1}$ . From a comparison of the edge positions at zero applied pressure, it is apparent that the induced shift cannot be due to a significant change of the Ce valence state. The energy difference between Ce K-edges for  $x = 3$  and  $3.5$  is  $0.6 \pm 0.3 \text{ eV}$ , whereas it is  $3.5 \pm 0.4 \text{ eV}$  between  $x = 3$  and  $5$ . This large change from  $x = 3$  to  $5$  is related to a difference in the valence of  $0.28 \pm 0.05$ , which has been estimated from a standard description [10] of the Ce  $L_3$ -edge data. The edge shift upon an applied pressure of  $40 \text{ GPa}$  ( $0.5 \pm 0.35 \text{ eV}$ ) has therefore approximately the same effect ( $0.6 \text{ eV}$ ) on the Ce valence as does a substitution of  $x = 0.5$  in the vicinity of the electronic substitutional phase transition. It is believed that the change in the Ce valence state is proportional to the shift in the Ce K-edge energy (chemical shift), and therefore the slight induced energy shift of  $0.5 \pm 0.35 \text{ eV}$  for an applied pressure of  $40 \text{ GPa}$  corresponds to change in valence of  $0.04 \pm 0.03e$  ( $0.12 \pm 0.09e$  of nominal oxidation state). This indicates that an effect of pressure on the valence is present but is unexpectedly small.

The observation of only a small energy shift in the absorption spectra is in accord with the results of the pressure dependence of the structure, which do not exhibit any deviations from a normal compression. For comparison, the pressure dependence of the Ce K-edge of  $\text{CeO}_2$  is also shown in figure 8. From a linear fit, no edge shift for increasing pressure is seen as expected for Ce in its nominal  $4+$  oxidation state. Note that very small differences have also been found with pressure at the Ce  $L_3$ -edge which are associated with the increase in covalency



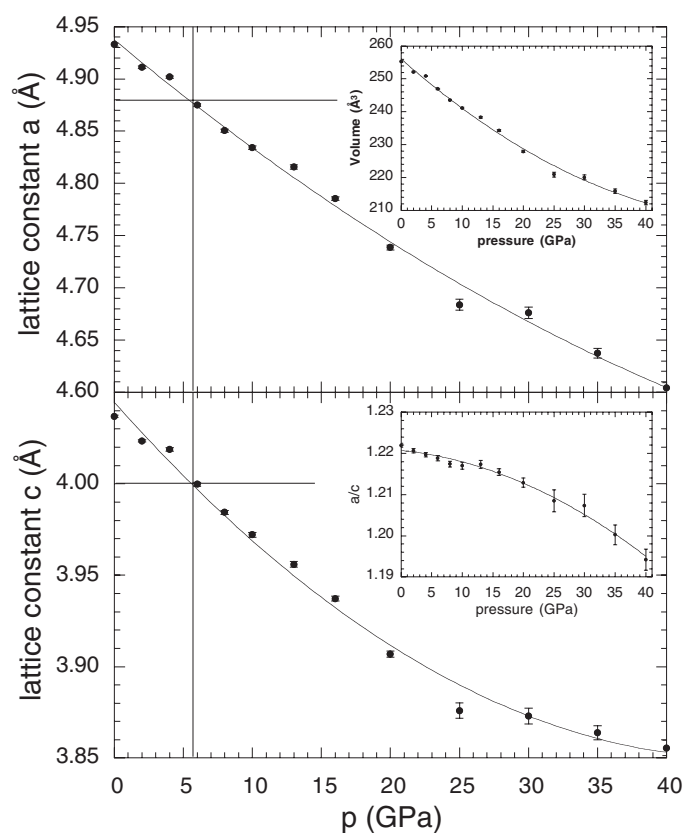
**Figure 2.** Image plate data taken at ID9 from  $\text{CeNi}_3\text{Cu}_2$  at 8 GPa. The black specks originate from diffraction in the diamond anvil cell and are excluded in the integration to obtain a one-dimensional powder diffraction pattern.



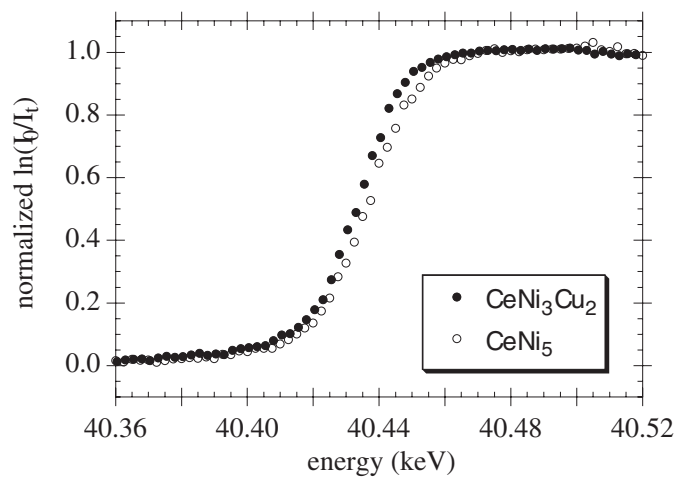
**Figure 3.** X-ray diffraction pattern (full curve), Rietveld refinement (small broken curve), background (large broken curve) and residuals (dotted curve) of  $\text{CeNi}_3\text{Cu}_2$ , taken at 8 GPa and with  $\lambda = 0.30433 \text{ \AA}$ .

and not with the increase in valence [11].

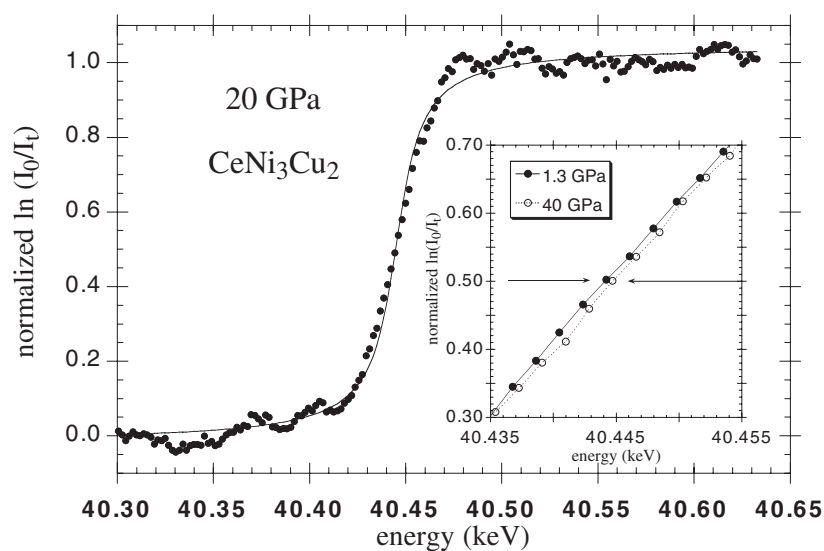
It is quite interesting that applying an external pressure of 40 GPa does not cause a stronger effect on the valence state, as would be expected in view of the fact that the substitution of Ni



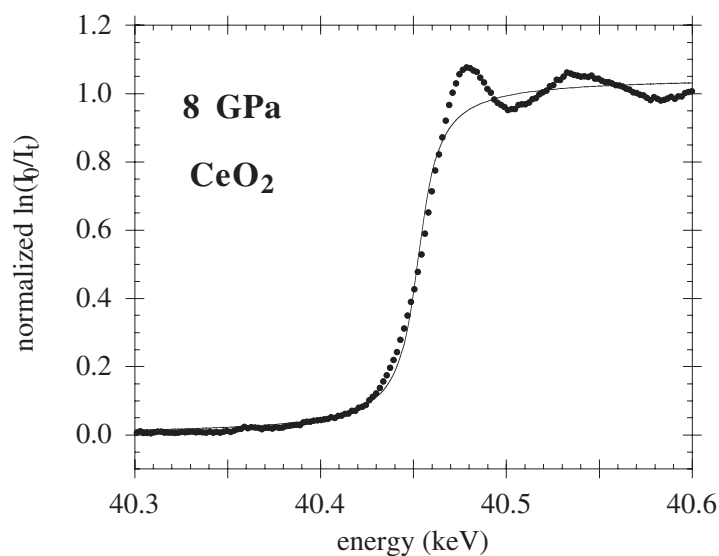
**Figure 4.** Lattice constants  $a$  and  $c$  of  $\text{CeNi}_3\text{Cu}_2$  as a function of applied external pressure. Inset: unit cell volume and  $a/c$  ratio as a function of applied pressure. The curves through the data are guides to the eye and the vertical lines corresponds to the structural parameters of  $\text{CeNi}_5$ .



**Figure 5.** X-ray absorption spectra of the Ce K-edge of  $\text{CeNi}_3\text{Cu}_2$  and  $\text{CeNi}_5$  taken at ambient pressure in energy step mode at ID15.



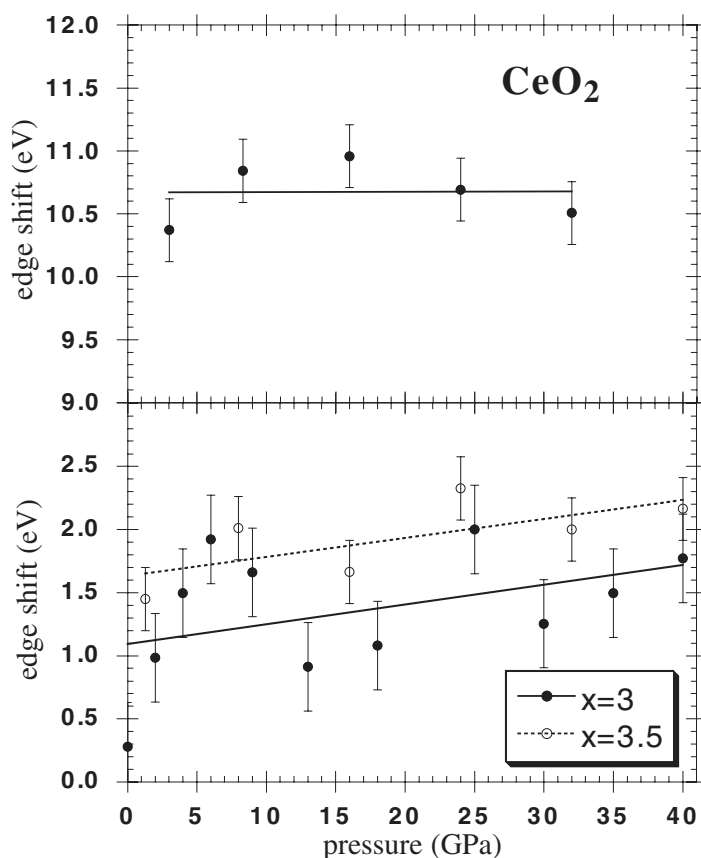
**Figure 6.** X-ray absorption spectra of the Ce K-edge of  $\text{CeNi}_3\text{Cu}_2$  taken at 20 GPa in dispersive mode. The curve corresponds to a fit to an arctan function. Inset: enlarged x-ray absorption spectra for 1.3 and 40 GPa to show the small energy shift.



**Figure 7.** X-ray absorption spectra of  $\text{CeO}_2$  taken at 8 GPa in dispersive mode.

by Cu leads to a reduction in the unit cell volume and therefore to a change from trivalent Ce to an intermediate valence state. The reduction in unit cell volume with pressure is much larger than the substitutional effect, indicating that the valence change is dominated by the electronic effect of shifting the Fermi surface closer to the 4f state energies, due to the different electronic states of Cu and Ni in these intermetallics.





**Figure 8.** X-ray absorption edge shifts of the Ce K-edge ( $\approx 40$  keV) for  $\text{CeNi}_x\text{Cu}_{5-x}$  (lower part) and  $\text{CeO}_2$  (upper part).

#### 4. Conclusion

The effect of external pressure up to 40 GPa leads to a 15% decrease in unit cell volume. The effect of pressure on the Ce valence state is approximately  $0.04e$  (nominal  $0.12e$ ), in contrast to the  $0.35e$  (nominal  $1.0e$ ) change from replacing Cu by Ni. The change in valence of Ce for Cu–Ni substitution is therefore due to the different electronic states of the Cu and Ni ions, and is little affected by the changes in the unit cell volume.

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