

# Lattice spacing and thermal expansion anomalies in the Laves compound, $\text{CeNi}_2$

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Lattice spacing and thermal expansion studies have been carried out on the cubic Laves compound  $\text{CeNi}_2$ . The lattice spacings are very dependent upon the thermal history of the material, and quenching from above  $\sim 500^\circ\text{C}$  results in a contraction of the room-temperature lattice spacing. The higher the quenching temperature the greater the contraction. Thermal expansion studies over the temperature range from 25 to  $725^\circ\text{C}$  indicate a substantial rise in the expansion coefficient at around  $500^\circ\text{C}$ . Above  $650^\circ\text{C}$  there is a marked softening of the sample, which contracts under the slight load of the transducer spring used in the dilatometer. Lattice spacing measurements of some  $\text{Ce}(\text{Ni}_{1-x}\text{Cu}_x)_2$  alloys show that very small additions of copper result in a sharp contraction of the lattice spacing. All these effects have been related to the critical electron concentration of  $\text{CeNi}_2$  and to the consequent generation of constitutional vacancies, either as a function of temperature or with alloy composition.

## 1. Introduction

The lattice spacing behaviour of the cubic (C15) Laves phase  $\text{CeNi}_2$  has been carefully examined in the authors' laboratory [1–3] together with the ternary alloys  $\text{Ce}(\text{Ni}_{1-x}\text{Co}_x)_2$  [3–6] and  $\text{Ce}(\text{Ni}_{1-x}\text{Fe}_x)_2$  [7]. These studies indicated an effective valency of around 3.4 for the cerium atoms in  $\text{CeNi}_2$ , a very sharp step in the lattice spacing variation with composition across the phase field of  $\text{CeNi}_2$ , and a collapse of the lattice spacing with very small additions of iron in the  $\text{Ce}(\text{Ni}_{1-x}\text{Fe}_x)_2$  alloys. The lattice collapse was only observed in the  $\text{Ce}(\text{Ni}_{1-x}\text{Co}_x)_2$  alloys on annealing the powdered alloys, and the effect disappeared for  $x < 0.77$ .

The lattice spacings of  $\text{CeNi}_2$  obtained in the various investigations in the authors' laboratory show very good agreement but the values reported by other workers [8–10] are close to the "collapsed" value characteristic of nickel contents slightly greater than that of  $\text{CeNi}_2$ . The various lattice spacings are summarized in Table I.

The lattice spacing behaviour across the  $\text{CeNi}_2$  phase field has been interpreted [3] in terms of an increase in the vacancy concentration for nickel contents above 66.67 at %. The difference in the values of the "as-crushed" and "annealed" lattice spacings was attributed to the effect of deformation on the structure of the alloy but the present work shows that the lattice spacing differences are, in fact, due to the different cooling rates of the samples from the annealing temperature.

A number of attempts [5–8, 10–16] have been made to define the electronic state of the cerium atoms in  $\text{CeNi}_2$  by a variety of experimental techniques, but a precise definition has not yet been attained.

The present work was undertaken in order to provide more information on the origin of the lattice spacing collapse within the  $\text{CeNi}_2$  phase field and in the  $\text{Ce}(\text{Ni}_{1-x}\text{Co}_x)_2$  and  $\text{Ce}(\text{Ni}_{1-x}\text{Fe}_x)_2$  ternary alloys. It is essential to fully characterize the structural nature of these alloys before attempting to interpret their physical behaviour, particularly with regard to the valency state of the cerium atoms.

## 2. Materials and experimental methods

The cerium metal was supplied by Rare Earth Products Ltd, and the copper and nickel by Koch Light Laboratories Ltd. The alloys were prepared by arc melting in a pre-gettered argon atmosphere. The arc-melted buttons were homogenized by annealing in a vacuum for 7 days at  $750^\circ\text{C}$ . After this treatment the homogeneity of the individual alloys was established by examining a polished section in a Philips 500 SEM using electron back-scattering and energy-dispersive X-ray analysis (EDAX).

The bulk  $\text{CeNi}_2$  alloys were quenched from a variety of temperatures using a specially constructed vacuum-quenching rig and then crushed to a fine powder which was exposed to  $\text{CoK}\alpha$  radiation in a Debye–Scherrer camera. Because of the very brittle nature of these alloys at room temperature, good quality diffraction patterns were obtained from the "as-crushed" powder though the quality of the patterns did depend upon the particular heat treatment of the bulk alloys.

The thermal expansion measurements were obtained using a carefully calibrated LVDT–silica push-rod system and the sample was in the form of a cylinder, approximately 0.5 cm long with flat parallel ends. The sample could be heated and cooled in a linear fashion over the temperature range 25 to  $1000^\circ\text{C}$  in a good

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TABLE I The lattice spacings of CeNi<sub>2</sub> as reported by several authors

Lattice spacing (nm)	Reference
0.7202	Wernick and Geller [9]
0.7197	Wallace <i>et al.</i> [10]
0.7206	Olcese [8]
0.72237	Mansey <i>et al.</i> [1]
0.72246	Mansey <i>et al.</i> [4]
0.72246	Harris and Longworth [7]
0.72250	Brochado Oliveira and Harris [5]
0.72050	Harris and Brochado Oliveira [3]
0.7209* (32.5 at % Ce)	Harris and Longworth [7]

\*Extrapolated value from lattice spacing variation in the Ce(Ni<sub>1-x</sub>Fe<sub>x</sub>)<sub>2</sub> system.

vacuum. In the present measurements a linear heating and cooling rate of 10°C min<sup>-1</sup> was employed.

### 3. Experimental results and discussion

#### 3.1. The lattice spacings of CeNi<sub>2</sub> after various quenching treatments

In view of our previous observations [3] on the lattice spacing variation across the CeNi<sub>2</sub> phase field it is important to establish whether the lattice spacing of CeNi<sub>2</sub> is sensitive to the heat treatment of the alloy. Hence, in the present work, the lattice spacings of CeNi<sub>2</sub> have been examined after a series of heat treatments which consist of annealing the bulk alloys for 1 h at a variety of temperatures within the range 200

to 750°C and then quenching to room temperature. The solid specimen was then crushed to a fine powder for X-ray examination.

The variation of the room-temperature lattice spacing as a function of the annealing temperature is shown in Fig. 1. The variation clearly shows that the lattice spacing of CeNi<sub>2</sub> is very dependent upon its thermal history and Fig. 1 shows a small maximum in the *a*-spacing at around 450°C, followed by a marked contraction which appears to be levelling out around 750°C. On quenching from 500°C and above, there is a significant deterioration in the quality of the diffraction patterns and broader lines are obtained. This is reflected in the larger error bars (as indicated by the least-squares fit) associated with the lattice spacing measurements, and these are shown in Fig. 1.

The magnitude of the fall in lattice spacing shown in Fig. 1 is very similar to that observed in the "step-like" lattice-spacing variation across the phase of CeNi<sub>2</sub> [3] (Fig. 2). The difference between the lattice spacings of the "as-crushed" material from the bulk alloy and that of the annealed powder [3] can now be attributed to the faster cooling rate of the annealed powder rather than to the influence of the deformation process as speculated in our previous paper [3]. Thus the annealed powder was subject to a faster cooling rate than the bulk alloy, giving the contracted lattice spacing. A similar argument can also be applied to the lattice spacing behaviour of the Ce(Ni<sub>1-x</sub>Co<sub>x</sub>)<sub>2</sub> alloys reported in the same work [3].

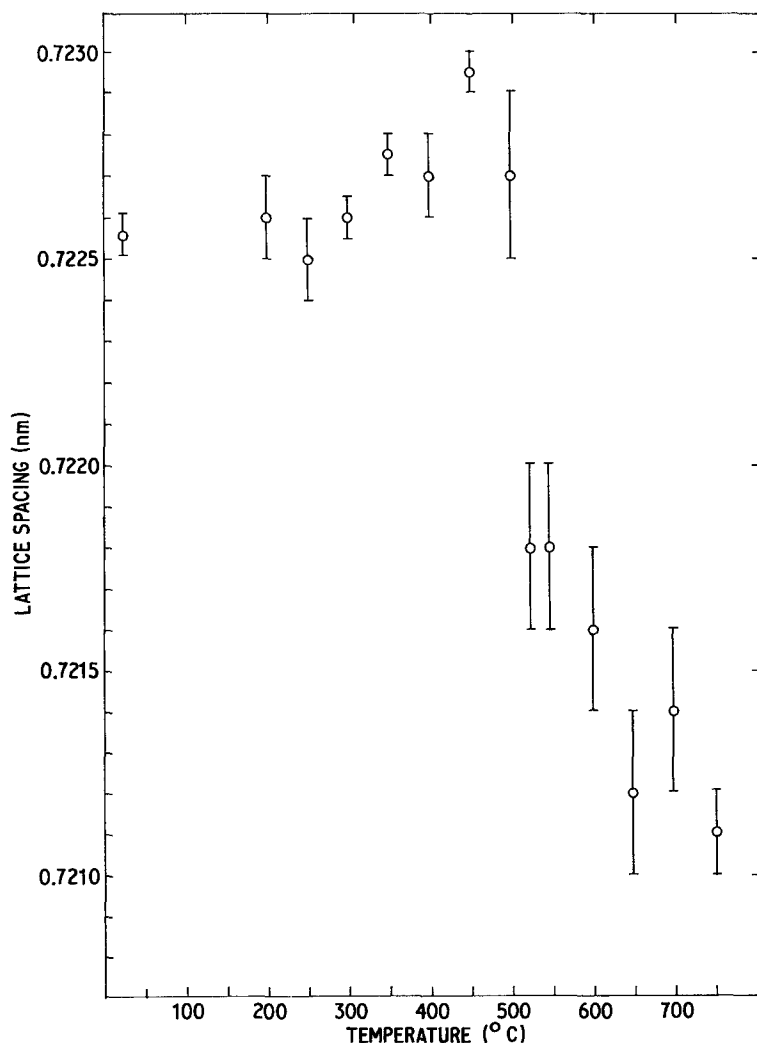


Figure 1 The variation of the room-temperature lattice spacing as a function of the annealing temperature. The bulk specimens were annealed for 1 h at the various temperatures and then quenched to room temperature.

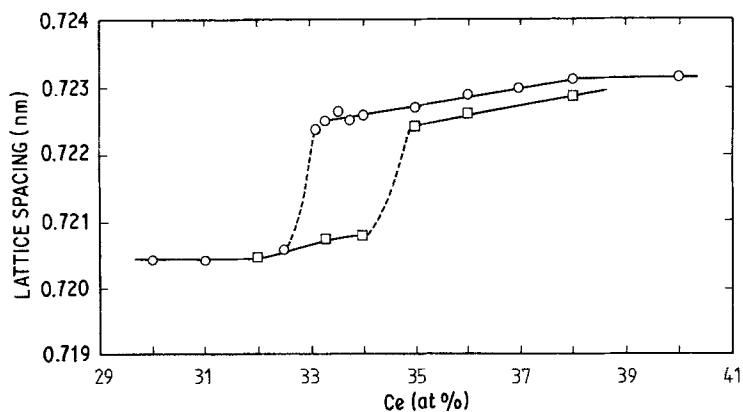


Figure 2 The variation of the room-temperature lattice spacings across the phase field of  $\text{CeNi}_2$ : (○) lattice spacings of "as-crushed" powder; (□) lattice spacings of annealed powder (quickly cooled from  $600^\circ\text{C}$ ).

The very unusual lattice spacing behaviour shown in Fig. 1 can largely be ascribed to the presence of constitutional vacancies in the lattice of  $\text{CeNi}_2$ , the concentration of which is strongly temperature-dependent above  $500^\circ\text{C}$ . Thus, on quenching from high temperatures, large concentrations of vacancies are retained in the lattice with a consequent collapse of the lattice spacing. The higher the quenching temperature the greater is the retained vacancy concentrations and the greater is the lattice contraction. It should be noted here that the proposed change in the vacancy concentration in  $\text{CeNi}_2$  could also have an influence on the effective valency of the cerium atoms, which would also affect the lattice spacing behaviour. The origin of the maximum in the lattice spacing variation shown in Fig. 1 is not known, but the temperature of this maximum does correspond with that of the "levelling-out" of the  $\Delta l/l$  values in the expansion curve (see later).

In a previous paper [5] we suggested that the cerium atoms had an effective valency of 3.4 in  $\text{CeNi}_2$ , which gives an electron concentration for this phase which is at the proposed [10, 17] limit of stability for the cubic Laves structure. Thus it was suggested [5] that the effective valency of the cerium atoms was the maximum allowable on the basis of phase stability. These arguments are consistent with the present work, indicating the generation of constitutional vacancies at high temperature. It is known that these vacancies are formed as the means of perpetuating phase stability in alloys which have attained a critical electron concentration. Well-known alloys of this kind are those based on the  $3/2$  electron compounds  $\text{NiAl}$  [18, 19] and  $\text{PdIn}$  [20, 21], where constitutional vacancies are found on the transition metal sites at compositions in excess of 50 at % Al and 50 at % In, respectively. The present observations can therefore be interpreted in terms of the high-temperature phase stability of  $\text{CeNi}_2$  being perpetuated by the generation of constitutional vacancies. If this is the case then the surprisingly marked temperature dependence of the phase stability of  $\text{CeNi}_2$  could be associated with the unstable valency state of the cerium atoms. It is not clear at this stage, however, why the stability of this phase could not be controlled solely by "valency compensation".

### 3.2. The thermal expansion of $\text{CeNi}_2$

If, as suggested by the lattice spacing behaviour out-

lined in Section 3.1, there is an unusually high vacancy concentration in  $\text{CeNi}_2$  at temperatures above  $450^\circ\text{C}$ , then thermal expansion anomalies would be anticipated in this alloy. Thus the thermal expansion behaviour of a  $\text{CeNi}_2$  alloy has been examined over the temperature range from room temperature to  $725^\circ\text{C}$  at a linear heating and cooling rate of  $10^\circ\text{C min}^{-1}$ .

Two  $\text{CeNi}_2$  samples were investigated, one of which had been annealed at  $600^\circ\text{C}$  and then slowly cooled to room temperature whereas the other had been quenched from  $600^\circ\text{C}$ . The variations of  $\Delta l/l$  against  $T$  are shown in Fig. 3 (where  $\Delta l$  is the length change and  $l$  the room-temperature length of the specimen) and the significant features of these curves are:

- (i) the close similarity in expansion behaviour of both samples up to  $\sim 500^\circ\text{C}$ ;
- (ii) the levelling out of the  $\Delta l/l$  values around  $450^\circ\text{C}$  (for the slowly cooled sample);
- (iii) the marked increase in the expansion coefficient  $\alpha$  at around  $500^\circ\text{C}$ ;
- (iv) the more rapid rise in  $\alpha$  for the slowly cooled sample; and
- (v) the marked contraction of the quenched sample beginning at around  $650^\circ\text{C}$ .

The expansion effects (i), (iii), (iv) and (v) outlined above are consistent with the proposed constitutional vacancy model used to explain the lattice spacing behaviour. The "levelling-out" of the expansion curve occurs at a temperature close to that of the lattice spacing maximum shown in Fig. 1. The temperature of the onset of the expansion anomaly is very close to the onset of the rapid fall in the lattice spacing against quenching temperature curve shown in Fig. 1. The expansion behaviour above  $500^\circ\text{C}$  can be interpreted in terms of a marked increase in the vacancy concentration above this temperature which results in a large additional contribution to the expansion of the alloy. This expansion effect should correspond with a decrease in the density of the sample. The much smaller expansion anomaly observed in the case of the quenched alloy is consistent with the high concentration of retained vacancies in this sample as shown by the lattice spacing measurements. The close agreement between the curves of the two samples up to  $\sim 500^\circ\text{C}$  shows that the retained vacancies in the quenched sample do not affect the expansion behaviour up to the critical temperature.\*

\* The thermal expansion behaviour of the neighbouring  $\text{PrNi}_2$  phase has also been investigated in the present work over the temperature range 25 to  $725^\circ\text{C}$ . A very regular expansion curve was observed with no evidence of any expansion anomalies or softening effects.

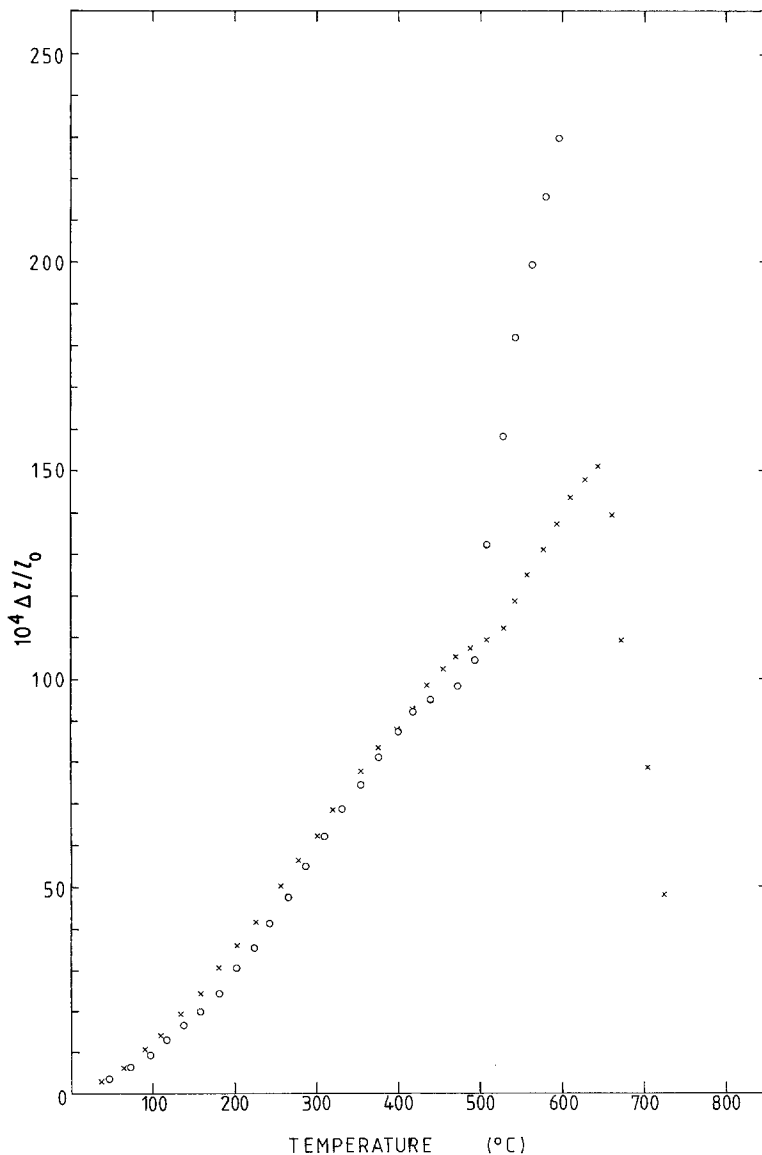


Figure 3 The variation of  $\Delta l/l$  against  $T$  for two  $\text{CeNi}_2$  samples: (O) annealed at  $600^\circ\text{C}$  and then slowly cooled to room temperature before measurements; (x) annealed at  $600^\circ\text{C}$  and then quenched before measurements.

The contraction of the quenched sample at  $T > 650^\circ\text{C}$  occurs under the slight compressive load of the transducer spring. This indicates a marked softening of the alloy at temperatures in excess of  $650^\circ\text{C}$  which is in stark contrast to the very brittle nature of  $\text{CeNi}_2$  at room temperature. The deformation is totally plastic in nature, and a pronounced change in sample shape is observed after the dilatometric measurements. The softening effect is also in accordance with the proposed high-temperature high vacancy concentration in the alloy, which allows the sample to readily change its shape under the action of the silica push-rod by a vacancy-assisted deformation process.

### 3.3. Estimates of vacancy concentrations in $\text{CeNi}_2$

The vacancy concentrations in  $\text{CeNi}_2$  above  $500^\circ\text{C}$  can be estimated from an analysis of the thermal expansion and lattice spacing behaviour. The dilatometric contribution of the vacancies is estimated by extrapolating the expansion curve in the range 150 to  $400^\circ\text{C}$  to the high-temperature regime and measuring the difference between the extrapolated and actual behaviour. This data together with the values of  $\Delta a/a$  are then used to calculate the vacancy concentration. Unfortunately the large errors in the lattice spacing

measurements on quenching from above  $500^\circ\text{C}$  means that only approximate values of the vacancy concentrations can be obtained.

The estimated vacancy concentration at  $600^\circ\text{C}$  is 2.1 at %.

### 3.4. The lattice spacings of some $\text{Ce}(\text{Ni}_{1-x}\text{Cu}_x)_2$ alloys

It has been suggested previously [3] that the collapse of the lattice spacing across the  $\text{CeNi}_2$  phase field at nickel contents very slightly greater than that of stoichiometry (66.67 at % Ni) is due to a sharp increase in the vacancy concentration with increasing nickel content. A similar, very abrupt fall was observed in the lattice spacing variation of some  $\text{Ce}(\text{Ni}_{1-x}\text{Fe}_x)_2$  alloys [7] on substituting a very small proportion of the nickel atoms by iron.

In the present work we have examined the lattice spacing behaviour of some  $\text{Ce}(\text{Ni}_{1-x}\text{Cu}_x)_2$  alloys in order to study the effect of adding copper on the lattice spacing of  $\text{CeNi}_2$ . The room-temperature lattice spacings of the alloys in the range  $0 \leq x \leq 0.15$  are shown in Fig. 4 and, as in the case of the  $\text{Ce}(\text{Ni}_{1-x}\text{Fe}_x)_2$  alloys described above, there is a very sharp fall in the lattice spacing on adding a very small amount ( $x < 0.03$ ) of copper to the alloy. Extrapolation

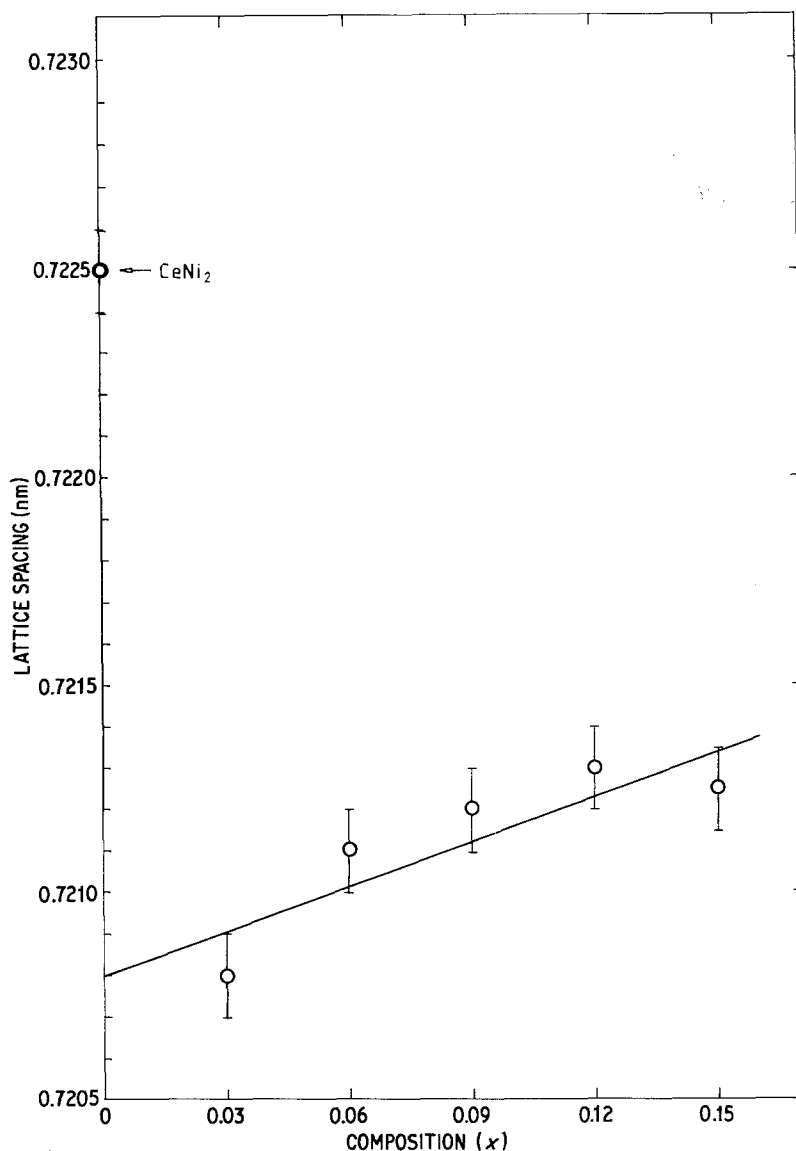


Figure 4 The variation of the room-temperature lattice spacings of some  $\text{Ce}(\text{Ni}_{1-x}\text{Cu}_x)_2$  alloys as a function of  $x$ .

of the lattice spacing variation to 0% Cu gives a lattice spacing of 0.7208 nm for  $\text{CeNi}_2$  which, within experimental limits, is identical both with the extrapolated value obtained from the variation of lattice spacings for the  $\text{Ce}(\text{Ni}_{1-x}\text{Fe}_x)_2$  alloys and with the "collapsed" value observed within the  $\text{CeNi}_2$  phase field (see Table I and Fig. 2). The present observations clearly indicate sufficient solubility of copper in the  $\text{Ce}(\text{Ni}_{1-x}\text{Cu}_x)_2$  alloys to cause the lattice spacing collapse, but additional X-ray reflections for  $x \geq 0.03$  indicate a limited solubility. Previous studies [10, 22] have also shown very limited solubility in this system.

### 3.5. General observations

The present and previous observations illustrate the very precarious state of the lattice spacing of  $\text{CeNi}_2$  which can be collapsed by heating to temperature in excess of  $450^\circ\text{C}$ , by very slightly increasing the nickel content or by substituting a very small proportion of the nickel atoms by either iron or copper. The effects are consistent with the proposed [5] critical state of  $\text{CeNi}_2$  but cannot be interpreted simply in terms of the changes in the electron concentration. Thus, the addition of copper to replace nickel would be expected to increase this factor, whereas the substitution of nickel by iron would normally be expected to decrease

the electron concentration. Clearly more work has to be done in order to understand the precise nature of  $\text{CeNi}_2$  at room temperature and how it is effected by modest rises of temperature, by very small changes in stoichiometry and by very small substitutions of the nickel atoms.

### 4. Conclusions

The main conclusions of the present work are as follows:

1. The lattice spacing of  $\text{CeNi}_2$  is very dependent upon the heat treatment, and quenching from above  $450^\circ\text{C}$  results in a contraction of the room-temperature lattice spacing.
2. A pronounced thermal expansion anomaly occurs in  $\text{CeNi}_2$  at  $T \sim 500^\circ\text{C}$  and the effect is much larger in a sample which has been slowly cooled from high temperatures than in a quenched sample.
3. The lattice-spacing and thermal-expansion behaviours are consistent with the generation of constitutional vacancies at temperatures in excess of  $500^\circ\text{C}$ .
4. There is a marked softening of  $\text{CeNi}_2$  at high temperatures and this has been ascribed to the high vacancy concentration giving rise to a vacancy-assisted deformation process.

5. The lattice spacings of some  $Ce(Ni_{1-x}Cu_x)_2$  alloys show a sharp contraction on substituting a very small proportion of the nickel atoms by copper. This behaviour, and that observed in  $Ce(Ni_{1-x}Fe_x)_2$  alloys and nickel-rich  $CeNi_2$  alloys, has been ascribed to the onset of constitutional vacancies.

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