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Valency compensation in the Laves system, $Ce(Co_{1-x}Ni_x)_2$

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The pseudo-binary systems $Ce(Co_{1-x}Ni_x)_2$ (and for comparison, $Zr(Co_{1-x}Ni_x)_2$), $0 \leqslant x \leqslant 1.0$ have been studied by means of magnetic susceptibility measurements and by room-temperature X-ray diffraction. The experimental data indicate that the electronic state of cerium in the $Ce(Co_{1-x}Ni_x)_2$ alloys is variable as a function of composition, and the behaviour is interpreted on the basis of a comparison with the similar system $Zr(Co_{1-x}Ni_x)_2$ in which zirconium is regarded as a stable tetravalent element. A limit in the stability of the Laves phase in the $Zr(Co_{1-x}Ni_x)_2$ system has been found at $x \simeq 0.76$ (~ 51 at% Ni); this behaviour is interpreted in terms of the electron concentration reaching a maximum value for the stability of the cubic Laves phase structure in these alloys. The Laves phases in the $Ce(Co_{1-x}Ni_x)_2$ alloy system form a complete solid solution; this behaviour is interpreted in terms of the stability of the structure being maintained across the whole composition range by changes in the effective valency of the cerium atoms as the cobalt atoms are substituted by nickel, i.e. a "valency compensation" effect. From a comparison with the lattice parameter of the $Zr(Co_{1-x}Ni_x)_2$ alloys it was possible to determine an approximate value of 3.4 for the effective valency of cerium in the $CeNi_2$ phase.

1. Introduction

The phase relationships in a number of pseudobinary systems involving rare earth Laves compounds have been studied by several workers (see for example [1, 2]). The cerium-containing systems have proved of great interest as the electronic state of cerium is very sensitive to its alloying environment and in different alloy systems it is possible to obtain cerium valency states varying from 3.0 ($4f^1$) to 4.0 ($4f^0$). For instance Harris and co-workers [3, 4] have studied the electronic state of cerium in the complete solid solution, Cu_3Au-type pseudo-binary system $Ce(Rh_{1-x}Pd_x)_3$ and showed that the progressive reduction in the cerium valency at $x > 0.8$ compensates for the increase in the electron concentration due to the substitution of rhodium by palladium, and this process was responsible for the maintenance of the Cu_3Au-type structure across the entire composition range. A comparison of the electronic and crystal structure of the $Ce(Rh_{1-x}Pd_x)_3$ alloys and the $Zr(Rh_{1-x}Pd_x)_3$ alloys [4] provides very convincing confirmation of the cerium behaviour.

Mansey *et al.* [5] investigated the lattice spacings of a number of pseudo-binary systems of the cubic Laves phase formed by rare earth metals with iron, cobalt, nickel and rhodium. Large negative deviations from ideal behaviour of the lattice spacings were observed in the systems $Ce(Fe_{1-x}Ni_x)_2$ and $Ce(Co_{1-x}Ni_x)_2$ whereas large positive deviations were exhibited in such systems as $Er(Fe_{1-x}Co_x)_2$ and $Er(Fe_{1-x}Ni_x)_2$. In other cases such as $Pr(Co_{1-x}Ni_x)_2$ the deviations were small and positive. In $CeFe_2$ and $CeCo_2$ the cerium appears to adopt the 4-valent state, while the behaviour of the $CeNi_2$ phase was interpreted in terms of the valency state of the cerium atoms being intermediate between 3.0 and 4.0.

Harris and Longworth [6, 7] made very detailed

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X-ray and ^{57}Fe Mössbauer studies on a series of alloys in the pseudo-binary systems $Ce(Fe_{1-x}Ni_x)_2$ and $Ce(Fe_{1-x}Co_x)_2$. They noted that in the former system, in the range $x = 0$ to $x = 0.5$, the variation of the room temperature lattice spacing of the cubic Laves phase with increasing nickel content was similar to that observed in the system $Ce(Fe_{1-x}Co_x)_2$ with increasing cobalt content. Substantial positive deviations from the $Ce(Fe_{1-x}Co_x)_2$ curve however, were observed at values of $x > 0.5$ and these have been interpreted in terms of a decrease in the effective valency of the cerium atoms from the initial value of 4.0 ($4f^0$).

The pseudo-binary system $Ce(Co_{1-x}Ni_x)_2$ is a particularly suitable system for studying the influence of the alloying environment on the electronic state of cerium. A simple comparison with other isostructural systems suggests that the valency state of cerium in the $Ce(Co_{1-x}Ni_x)_2$ system is a function of composition. In the $Pr(Co_{1-x}Ni_x)_2$ and $Er(Co_{1-x}Ni_x)_2$ systems the valence state of the rare earth metal is stable and the lattice spacing variation [5] shows a small positive deviation from ideality which contrasts with the large negative deviation in the cerium system. Furthermore, in the absence of any change in the electronic state of the rare earth atoms, the variation of lattice spacing in both systems is determined by the effective sizes of the transition metals which, for cobalt (0.2504 nm) and nickel (0.2492 nm), are almost identical. Thus, from simple size considerations alone, the lattice spacing of $CeNi_2$ should be slightly less than that of $CeCo_2$, similar to the difference observed between $ErCo_2$ and $ErNi_2$ or between $PrCo_2$ and $PrNi_2$ where there is little possibility of a valency change.

As mentioned previously it was found that a comparison of the lattice spacing and magnetic susceptibility behaviour of the $Zr(Rh_{1-x}Pd_x)_3$ system [4] with that of $Ce(Rh_{1-x}Pd_x)_3$ proved to be very informative and hence the $Zr(Co_{1-x}Ni_x)_2$ system was also studied as a comparison with the corresponding cerium system. Zirconium should be in a stable 4-valent state and therefore, the behaviour of this system would be similar to that of $Ce(Co_{1-x}Ni_x)_2$ providing the cerium atoms maintain the quadrivalent state across the whole system.

Other workers have studied the valency state of cerium in $CeNi_2$ and these studies will be discussed in relation to the present work later in this paper.

2. Materials and experimental methods

The cerium metal was supplied by Rare Earth Products Ltd., and the cobalt, nickel and zirconium were supplied by Koch-Light Laboratories Ltd. The alloys were prepared by arc melting the appropriate quantities of the elements in a pre-gettered argon atmosphere. The arc-melted buttons were weighed immediately after removal from the arc furnace in order to detect any possible loss. The losses incurred on melting were in most cases less than 0.002 g for a 2.5 g sample. It could thus be assumed that the nominal and "as-cast" composition were, within the limits of experimental error, the same.

The $Ce(Co_{1-x}Ni_x)_2$ alloys with composition given by $0 \leqslant x \leqslant 0.17$ were homogenized in a vacuum annealing furnace for 7 days at 1023 K and the remainder for 6 days at 923 K. The $Zr(Co_{1-x}Ni_x)_2$ alloys were homogenized for 7 days with temperatures between 1173 and 1273 K. Some of the specimens in the $Ce(Co_{1-x}Ni_x)_2$ system were examined metallographically after grinding on successive grades of emery paper and then polishing with a preparation of diamond paste. The specimens were examined in the etched condition using a mixture of 15% nitric acid, 50% hydrochloric acid and 35% glycerol. Their microstructures were characterized as being predominantly single phase in character and the typical microstructure of the $CeNi_2$ alloys is shown in Fig. 1.

The lattice spacing data has been obtained using the standard Debye–Scherrer technique. The powders (in the as-crushed state) were exposed to Co*Kα* radiation in a Philips Debye–Scherrer camera, and the lattice spacings were derived from the diffraction patterns by conventional methods, using an extrapolation technique for the elimination of systematic errors.

The magnetic susceptibilities were measured by the Faraday method using a Sartorius Vacuum Electro-microbalance. Spherical specimens weighing about 0.5 g were used with platinum as a standard of comparison. Where necessary the results were corrected for ferromagnetic impurities by means of the Honda–Owen method.

3. Experimental results and discussion

3.1. The $Zr(Co_{1-x}Ni_x)_2$ alloy system

3.1.1. X-ray diffraction results

The room temperature lattice spacings of the $Zr(Co_{1-x}Ni_x)_2$ alloy system are plotted as a func-

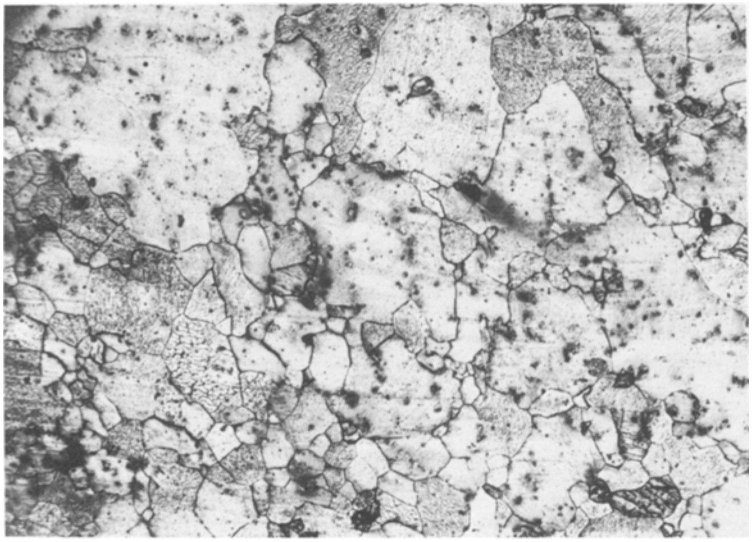

Figure 1 Photomicrograph of the $CeNi_2$ alloy (X 72).

tion of nickel concentration (expressed as x) in Fig. 2. The diffraction patterns show the appearance of extra lines in addition to those characteristic of the cubic Laves structure, for the nickel-rich alloys at $x > 0.73$.

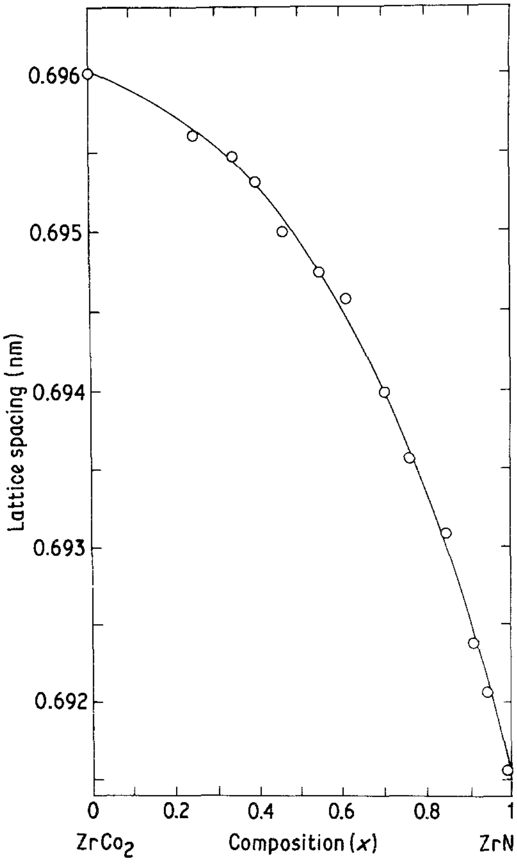

Figure 2 The room temperature lattice spacings of some $Zr(Co_{1-x}Ni_x)_2$ alloys.

The lattice spacing curve shows a positive deviation from the ideal behaviour with a maximum deviation at about $x = 0.45$.

3.1.2. Magnetic susceptibility results

The room temperature magnetic susceptibilities of some $Zr(Co_{1-x}Ni_x)_2$ alloys are shown in Fig. 3. It reveals a distinct break in the linear behaviour at $x \simeq 0.76$ (51 at% Ni). For $x > 0.76$, the magnetic susceptibility, χ, is practically invariant, with composition. The alloys with composition given by $x = 0.3$ and 0.405 exhibited strong field dependence; the other alloys have shown weak or medium field dependences. The susceptibility–temperature dependence was also determined for the $ZrCo_2$ and $ZrNi_2$ alloys (Figs. 4 and 5). The former exhibits a marked negative variation of χ with T, while $ZrNi_2$ exhibits a small positive variation. There is no observation of any Curie–Weiss behaviour for either phase and this was predicted from the absence of any localized electrons in these phases.

A change in magnetic properties can reveal some details of the $N(E_F)$, density of states at the Fermi level. Taniguchi *et al.* [8] were the first to make a systematic investigation of the 3d, 4d and 5d paramagnetic transition metals and alloys. By a suitable choice of alloy components, they measured the variation in susceptibility with electron concentration for b c c transition metal alloys. Their analysis of results was based on the Stoner equation:

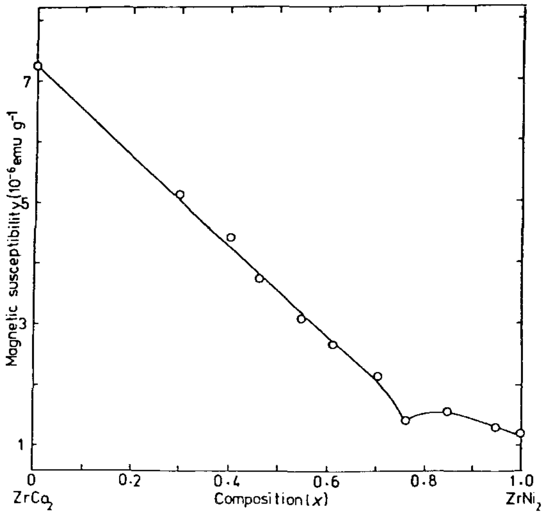

Figure 3 The variation of the magnetic susceptibility with composition, at room temperature, in the $Zr(Co_{1-x}Ni_x)_2$ system.

$$\chi_s = 2\mu_B^2 N(E_F)\left[1+\frac{\pi^2}{6}(kT)^2\gamma(E_F)\right]$$

with

$$\gamma(E_F) = \left[\frac{1}{N}\frac{\partial^2 N}{\partial E^2} - \left(\frac{1}{N}\frac{\partial N}{\partial E}\right)^2\right]_{E_F}$$

where $N = N(E)$, E_F is the Fermi energy and μ_B the Bohr magneton. Thus the Pauli spin paramagnetism is a direct measure of the density of states at the Fermi level $N(E_F)$ [9]. A close relationship between the shape of the density of state against electron concentration curve and the sign of $d\chi/dT$ has been observed, namely that $d\chi/dT > 0$ near a minimum in the density of states curve and $d\chi/dT < 0$ near a maximum in the same curve, thus confirming the observations of Kriessman and Callen [10].

The coefficient of the electronic heat capacity, γ, being directly proportional to $N(E_F)$, also offers very direct information on the electronic structure. Heiniger *et al.* [11] compiled a large amount of specific heat data from transition elements and made a plot of the γ against electron concentration in which it can be seen that, in the range of electron concentrations 7.3 to 8*, $N(E_F)$ decreases with a shallow minimum at about 7.8.

The magnetic data of the $Zr(Co_{1-x}Ni_x)_2$ system is consistent with this model so that, when nickel atoms substitute for cobalt atoms in the $ZrCo_2$ phase, the Fermi level increases, but $N(E_F)$ decreases continuously until it reaches a minimum at an electron concentration equal to 7.84, where the break in the approximately linear behaviour of the susceptibility occurs. The small positive slope $d\chi/dT$ observed at $ZrNi_2$ indicates a minimum in the density of states around that composition.

The influence of electronic factors is of particular significance in Laves phases in determining both the type of structure and the range of stability. Measurements of the changes in magnetic susceptibility [12] and electronic specific heat [13] of several alloys within the pseudo-binary systems, such as $MgCu_2$–$MgZn_2$, $MgNi_2$–$MgZn_2$, $MgCu_2$–$MgAl_2$, $MgZn_2$–$MgAl_2$ and $MgCu_2$–$MgSi_2$ indicate that a low density of states is

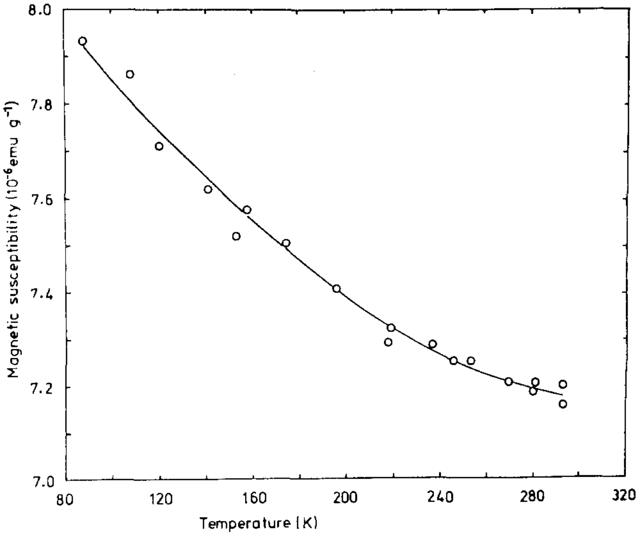

Figure 4 The variation of magnetic susceptibility with temperature of $ZrCo_2$.

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*Taking all the electrons outside the closed shells.

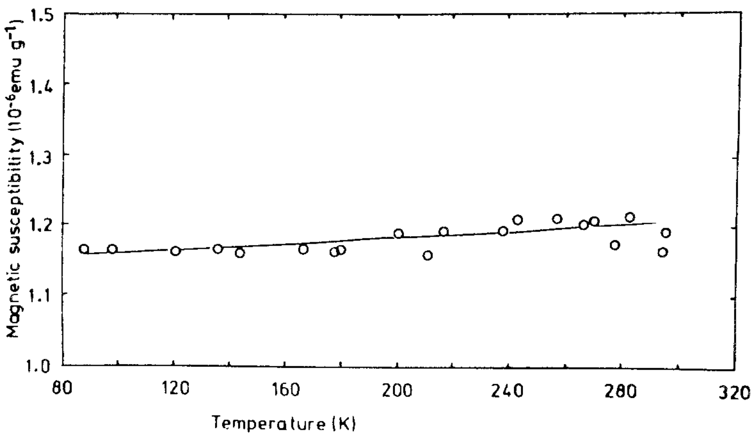

Figure 5 The variation of the magnetic susceptibility with temperature of $ZrNi_2$.

associated with phase boundaries and termination of solubility.

The work of Osterreicher and Wallace [14] on the $Gd(Co_{1-x}Al_x)_2$ and $Er(Co_{1-x}Al_x)_2$ systems and of Wallace *et al.* [15] on $Gd(Ni_{1-x}Cu_x)_2$ system and a large number of systems [16] represented by the formula $R(Ni_{1-x}Al_x)_2$, where R denotes a particular rare earth, indicates that the cubic, *C*15 structure for RNi_2 or RCo_2 became unstable and no longer could be formed for an electron at atom ratio (e/a) greater than about 1.15. This result has been interpreted in terms of Brillouin zone filling effects [17].

The criteria for establishing the contribution of the transition metal to the electron concentration, adopted by the above mentioned authors, were the ones that have been described by Wallace and Craig [13], namely:

(i) If the substance exhibits a local moment, the electrons involved in establishing that moment are excluded from the e/a.

(ii) If there is a component which in the elemental form has a local moment, but due to electron transfer, this moment in an alloy has been reduced to zero, the d-electrons are assumed to have remained localized and are excluded from consideration in establishing the e/a.

(iii) The electrons involved in establishing the local moment are estimated from the magnitude of the atomic moment.

On the basis of these criteria the phase $ZrNi_2$ would have an e/a of 1.33 and so should not exist in the cubic Laves structure [17], as this is beyond the stability range for the RNi_2 and RCo_2-based ternaries referred to above.

It is interesting to recall that Bardos *et al.* [18], in discussing the ternary Laves phases with transition elements and silicon, have related the occurrence of Laves phases as a group to the existence of an average e/a less than 8, when the total number of electrons outside of the rare gas core is considered. According to this, $ZrNi_2$ would have an e/a of 8 and so should not exist as a Laves phase.

Bsenko [19] studied the phase diagram of the Zr–Ni system in the region 65–80 at % Ni and concluded that the compound $ZrNi_2$ does not exist as a single phase cubic Laves structure. However, he observed that this structure could be formed if the $ZrNi_2$ alloy reacted with the silica containing tube giving rise to a ternary compound. This would be consistent with the silicon acting as an electron acceptor.

The diffraction pattern of the $Zr(Co_{1-x}Ni_x)_2$ alloys show the existence of extra lines for the nickel-rich alloys ($x \geqslant 0.76$). Although the lattice spacing measurements do not exhibit a steady value for the cubic Laves phase in the nickel-rich compositions, the precipitation of an extra phase over this range, clearly indicates that the hypothetical $ZrNi_2$ phase is non-stoichiometric in nature, which is consistent with the analysis referred to above.

The critical value of the electron concentration for the stability of the cubic $Zr(Co_{1-x}Ni_x)_2$ system that occurs at $x \simeq 0.76$ can be compared with the one suggested by Shidlovsky and Wallace [17] for the stability of the *C*15 structure RNi_2 or RCo_2, by assuming that the contribution of cobalt and nickel to the electron concentration in the $Zr(Co_{1-x}Ni_x)_2$ alloys is the same as that of cobalt in $ZrCo_2$ [13] and nickel in hypothetical $ZrNi_2$. Since on the Wallace and Craig criteria, 0.67 and 1.33 are the e/a values for $ZrCo_2$ and $ZrNi_2$, respectively, a value of 1.17 can be derived for the $x = 0.76$ alloy, which is in a fairly good agreement with the approximate value of 1.15 suggested for the limit of the stability of the cubic Laves phase [17].

Finally it appears from the magnetic susceptibility plot (Fig. 3) that if the linear decrease between $x = 0$ and $x = 0.76$ continued, a diamagnetic susceptibility would be obtained for the stoichiometric $ZrNi_2$ and this would indicate a filled d-band at this composition. Instead there is a local minimum at $x = 0.76$ after which there is no longer any linear behaviour and the susceptibility is practically invariant with composition. It may be argued that the precipitation of an extra phase in the range of composition $0.76 \leqslant x \leqslant 1$ could account for these differences in the magnetic properties. However, it seems unlikely because of the small amount of second phase as estimated by X-ray analysis. A more likely possibility is that the hypothetical $ZrNi_2$ phase is non-stoichiometric in nature at $x \geqslant 0.76$ and the maintenance of the Laves structure is dependent on a lower electron concentration which results in the presence of some d-bonding in the alloy.

It has been suggested [6] that the presence of vacant d-states is a necessary prerequisite for the existence of the Laves phase in the rare earth Group VIII systems and that the very limited occurrence of MPd_2 Laves phases (where M is another metal) could be due to the strong propensity of palladium to adopt the $4d^{10}$ configuration on alloying. A similar argument could be advanced to explain the phase stability in the $Zr(Co_{1-x}Ni_x)_2$ alloys.

3.2. The $Ce(Co_{1-x}Ni_x)_2$ alloy system

3.2.1. Lattice spacing measurements

The room temperature lattice spacings of a series of alloys in the pseudo-binary system $Ce(Co_{1-x}Ni_x)_2$ $0 \leqslant x \leqslant 1.0$, are plotted as a function of x in Fig. 6.

In earlier work in the authors' laboratory [5] the lattice spacing of a few alloys in the same system were also measured and reasonable agreement has been obtained between these results and the present spacing data for alloys of the same composition (see Fig. 6). The much greater number of alloys investigated in this work, however, has made it possible to determine the fine details of the spacing/composition curve. The measurements of the lattice spacings of some alloys which were prepared 4 years earlier are also included in Fig. 6. It appears that there are no significant differences between these results and those obtained by measuring freshly prepared alloys.

The X-ray patterns of the crushed alloys exhibited only lines due to the cubic $C15$ Laves phase structure, with the exception of the $CeNi_2$ alloy where some weak extra lines were noticeable. A large negative deviation from additivity is a general feature of the curve of lattice spacings against composition. It is also clear that progressively steeper rises in lattice spacings occurs at composition for $x > 0.33$, and $x > 0.75$. This is best illustrated by the plot of da/dx against the concentration x (Fig. 7) obtained graphically from the slope of the lattice spacing/composition curve in Fig. 6.

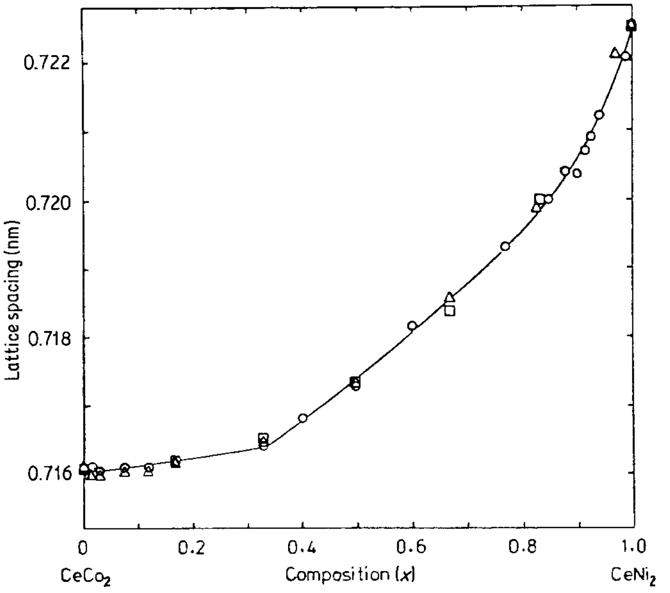

Figure 6 The variation of the room temperature lattice spacings with composition of $Ce(Co_{1-x}Ni_x)_2$ system: (○) present work, (□) previous work, [5]. The symbol (△) represents the lattice spacing obtained from alloys that were prepared 4 years earlier. (As-crushed values).

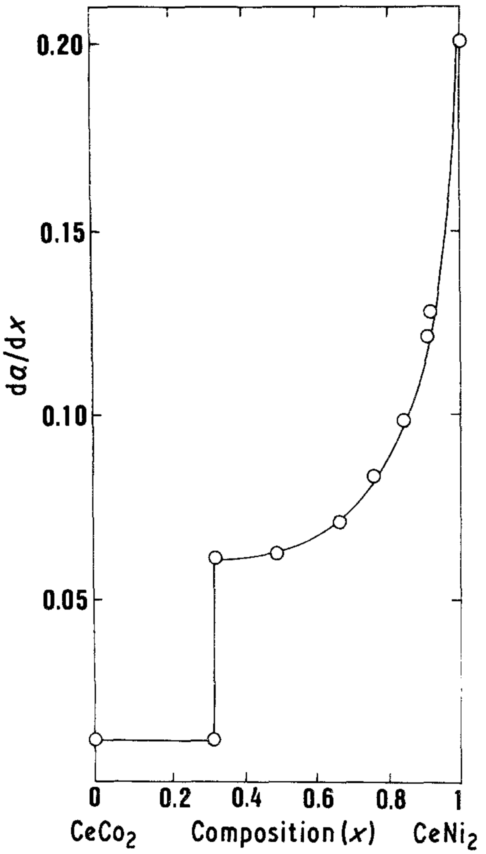

Figure 7 The variation of the derivative da/dx with x, where a is the lattice spacing (in nm) and x the mole fraction in Ce(Co$_{1-x}$Ni$_x$)$_2$.

3.2.2. Magnetic susceptibility measurements

The variation of the magnetic susceptibility with composition, at room temperature, in the Ce(Co$_{1-x}$Ni$_x$)$_2$ system is shown in Fig. 8. The measurements of the magnetic susceptibility of some alloys which were prepared 4 years earlier are also included in Fig. 8. It appears that there are some erratic but small deviations between these results and the ones obtained by measuring freshly prepared alloys. This may possibly be due to the differences in the state of purity of the two batches of cerium used in preparation of the samples or, more generally, to the differences in the small amount of contamination of ferromagnetic impurities that can occur on handling the alloys.

The dependence of the magnetic susceptibility with temperature was also studied for some alloys and the results are represented graphically in Figs. 9 and 10. These plots show that the alloys with composition $x = 0$, 0.12, 0.5 and 0.83 have a negative dependence of χ upon T (notably for CeCo$_2$) while the remaining alloys have a positive dependence. The alloys exhibited a weak or medium field dependence except for alloys at $x =$ 0, 0.015, 0.4 and 0.5 which showed a strong field dependence.

The variation of the room temperature magnetic susceptibility with composition (Fig. 8) shows two distinct parts. Thus from $x = 0$ to $x \simeq 0.33$ there is a marked decrease in χ, whereas from $x \simeq 0.33$ to $x = 1$, χ is practically invariant with composition with a slight minimum around $x = 0.9$.

These results can be interpreted in terms of a variable valency state of the cerium atoms in the pseudo-binary system Ce(Co$_{1-x}$Ni$_x$)$_2$ when cobalt is replaced by nickel. Thus, the electronic con-

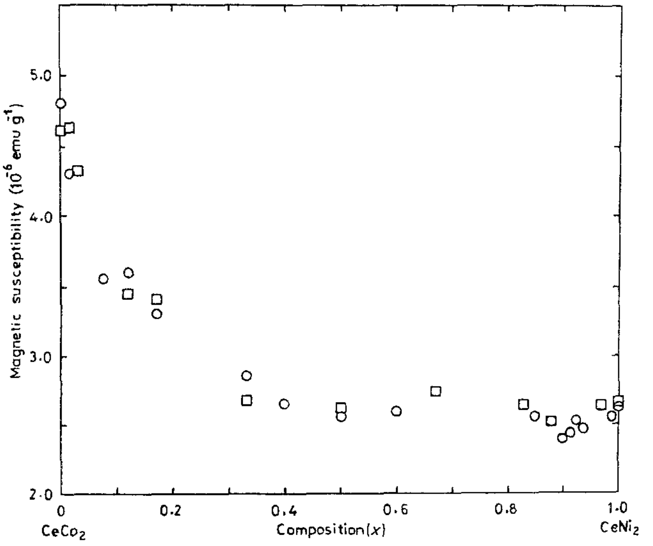

Figure 8 The variation of the magnetic susceptibility with composition at room temperature in the Ce(Co$_{1-x}$Ni$_x$)$_2$ system. (○) fresh samples; (□) 4 year old samples.

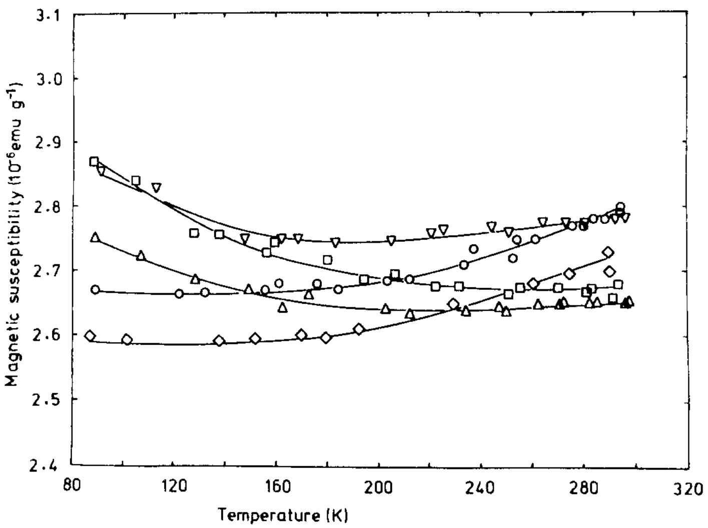

Figure 9 The variation of the magnetic susceptibility with temperature for some alloys in the $Ce(Co_{1-x}Ni_x)_2$ system. (○) $x = 1$; (◇) $x = 0.97$; (□) $x = 0.83$; (△) $x = 0.50$; (▽) $x = 0.33$.

figuration of cerium in the $CeCo_2$ compound is not very much affected by this substitution, until the fraction of nickel exceeds $x = 0.33$, as suggested by the lattice spacing behaviour. In $CeCo_2$ the 4f electrons of cerium have been transferred to the conduction band where the electrons are thought to occupy vacant levels in the 3d band [7]. Measurements of the low temperature specific heat and magnetic susceptibility in this compound [20] indicate that the 3d states are not completely filled and that there is a large exchange enhancement of the paramagnetic susceptibility.

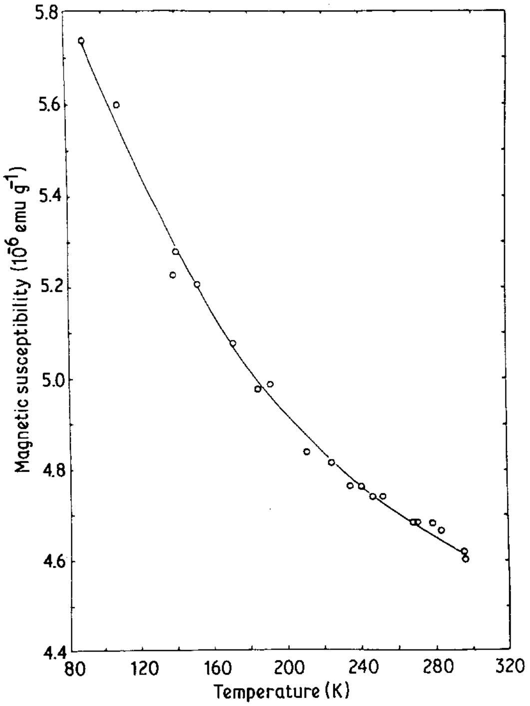

Figure 10 The variation of the magnetic susceptibility with temperature for the $CeCo_2$ alloy.

Smith and Harris [21] found that the $CeCo_2$ is a superconductor with a transition temperature at 0.84 K, whilst the $CeNi_2$ compound was found to remain normal to 0.15 K. The rather unexpected appearance of superconductivity in the $CeCo_2$ compound appears to be associated with the cerium atoms losing their 4f electrons to the cobalt d-band. This transition leaves both types of atom in a non-localized magnetic state and in addition provides a favourable electron per atom ratio for the occurrence of superconductivity [22].

The alloying behaviour of cerium in the $Ce(Co_{1-x}Ni_x)_2$ system can be interpreted on the basis of a comparison with that of the $Zr(Co_{1-x}Ni_x)_2$ system in which zirconium is a stable tetravalent element and there is no possibility of "4f effects" influencing the lattice spacing or magnetic susceptibility behaviour. Therefore, the magnetic susceptibility behaviour of the $Zr(Co_{1-x}Ni_x)_2$ system provides useful information about the conduction-band contribution to the total susceptibility of the $Ce(Co_{1-x}Ni_x)_2$ alloys. The marked fall in χ in the region $0 \leqslant x \leqslant 0.33$ can then be interpreted in terms of a rapid fall in $N(E_F)$ as observed in the $Zr(Co_{1-x}Ni_x)_2$ system (see Fig. 3). This is best illustrated by the plot of the normalized molar magnetic susceptibilities against composition for both the cerium and zirconium alloys represented in Fig. 11. Thus, in the range of compositions $0 < x < 0.33$ the magnetic susceptibilites of the $Ce(Co_{1-x}Ni_x)_2$ alloys decrease in a similar fashion to the $Zr(Co_{1-x}Ni_x)_2$ alloys and this is in agreement with the conclusion

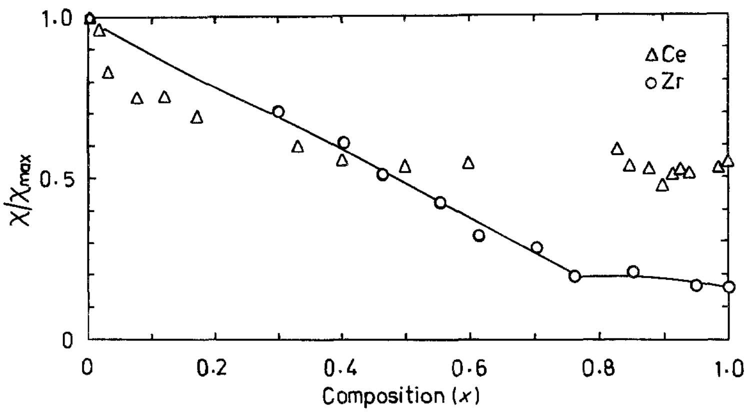

Figure 11 The normalized molar magnetic susceptibility as a function of composition for the $Ce(Co_{1-x}Ni_x)_2$ and $Zr(Co_{1-x}Ni_x)_2$ systems.

drawn from the lattice spacing data that the valence of the cerium atoms is maintained close to 4 for the initial nickel substitutions. For the alloys in which $x > 0.33$ the appearance of the 4f character is both supported by the marked increase in slope of the lattice spacing/composition variation and by the deviation of the magnetic susceptibility behaviour from that represented in the zirconium alloys. It can be suggested that the change in the electronic state of the cerium atoms results in a positive contribution to the paramagnetic susceptibility (as observed in the $Ce(Rh_{1-x}Pd_x)_3$ alloys at $x > 0.8$) [3] and this would compensate for the decreasing contribution from the density of states.

As already mentioned in the discussion of the results on the $Zr(Co_{1-x}Ni_x)_2$ alloys, studies of a large number of ternary Laves phases between the lanthanides and the d-transition metals make it clear that the *C*15 phase is unstable at electron concentration in excess of about 1.15. Viewed in this context the non-existence of stoichiometric $ZrNi_2$ was understood, and so was the existence of a limit in the $Zr(Co_{1-x}Ni_x)_2$ system for the stability of the cubic Laves structure. This limit was observed for the ternary alloys in which $x \simeq 0.76$ as revealed by X-ray diffraction patterns and magnetic susceptibility data, and so it was possible to determine the critical value of the electron concentration. Therefore, in the $Ce(Co_{1-x}Ni_x)_2$ system, it is proposed that the effective valency of the cerium atoms decreases with x in order to compensate for the increase in the total electron concentration due to the nickel additions, so that the critical value of the electron concentration for the stability of the cubic Laves structure is not exceeded. This "valency compensation" effect due to the increasing 4f population of the cerium atoms is also observed in other cerium containing systems such as $Ce(Rh_{1-x}Pd_x)_3$ [3] and $Ce(Fe_{1-x}Ni_x)_2$ [5] and in the case of the former system, allowed the Cu_3Au-type phase to be retained across the complete composition range.

The appearance of the slight minimum at $x \simeq 0.9$ could indicate a possible minimum in the density of states at the Fermi level, $N(E_F)$, at around this composition. This would be consistent with the change of sign of $d\chi/dT$ between $x = 0.97$ and $x = 0.86$ (see Figs. 9 and 10). The specific heat measurements on the $Ce(Co_{1-x}Ni_x)_2$ alloys [23] also support the above conclusion.

The magnetic susceptibility variation can be strongly influenced by the exchange enhancement term which is itself a function of $N(E_F)$. Thus a fall in $N(E_F)$ could be accompanied by a more pronounced decrease in the value of χ. Such an effect appears to occur in the $Ce(Co_{1-x}Ni_x)_2$ alloys [23].

The lattice spacing measurements on the pseudo-binary system $Ce(Fe_{1-x}Ni_x)_2$ by Harris and Longworth [6] reveals a change of slope at $x \simeq 0.5$ in the lattice spacing/composition curve, and a very sharp up-turn at $CeNi_2$. From a comparison with the lattice spacing behaviour of the $Ce(Fe_{1-x}Co_x)_2$ system they conclude that the cerium atoms maintain the 4-valent state ($4f^0$) up to $x \simeq 0.5$ and at $x > 0.5$ there was a change in the electronic state of the cerium atoms. The fact that, up to $x = 0.5$, the lattice spacings of the $Ce(Fe_{1-x}Ni_x)_2$ alloys closely follow those of the $Ce(Fe_{1-x}Co_x)_2$ system clearly shows that, in the absence of any change in the electronic state of the cerium atoms, the effect on the lattice spacings of substituting iron by nickel is similar to that of substituting iron by cobalt and this is quite consistent with the atomic diameter of nickel and cobalt. These workers [6] also concluded that the alloy Ce(FeNi) can be regarded as isoelectronic with the phase $CeCo_2$, and this would suggest that this binary phase represents a limiting case for the cerium atoms in the four valent ($4f^0$) state. This would be consistent with the very limited solubility, based on $CeCo_2$, exhibited in the system $Ce(Co_{1-x}Al_x)_2$ [5]. Therefore, the addition of nickel in the $Ce(Co_{1-x}Ni_x)_2$ alloys should lead to an immediate decrease in the effective valency of the cerium atoms, and this is shown by the immediate increase in the lattice spacing in this system at room temperature (Fig. 6). However, the magnetic susceptibility measurements discussed earlier indicate that if there is a change in the cerium valency in the range $0 \leqslant x \leqslant 0.33$, it is only slight.

In fact in the $Ce(Co_{1-x}Ni_x)_2$ system, the decrease in the effective valency of the cerium atoms with x is not uniform. There appears to be a more rapid decrease in the cerium valency at nickel compositions $x > 0.8$ which probably indicates that there is a gradual increase in the electron concentration with increasing nickel content (despite the valency change of the cerium atoms) and that a critical electron concentration is reached at the $x \simeq 0.8$ composition. The cubic Laves phase structure is then maintained by a more rapid decrease in the effective valency of the cerium atoms at greater nickel concentrations.

Assuming that the variation of the lattice spacing with composition of the $Ce(Co_{1-x}Ni_x)_2$ system, would be the same as that in the $Zr(Co_{1-x}Ni_x)_2$ system (see Fig. 2) providing the cerium was in a stable 4-valent state, then the expansion of the lattice due to the increase of the 4f population in the cerium atoms can be deduced. For example: the lattice spacing of $CeNi_2$ with cerium in a hypothetical quadivalent state should contract relative to $CeCo_2$ by the same amount ($\Delta a/a$) as $ZrNi_2$ contracts relative to $ZrCo_2$, namely 0.639%*. The actual lattice spacing of the $CeNi_2$ is however expanded relative to $CeCo_2$ by 0.893%. Thus the true lattice expansion relative to $CeCo_2$ due to the decrease of the effective valency of cerium in $CeNi_2$ can be taken as 1.53%. If the expansion of the lattice parameter observed in the $CeNi_2$ phase due to the proposed decrease in the effective valency of cerium is compared with the similar expansion observed in other cerium-containing systems where the valency state is known, it is possible to estimate the valency state of cerium in $CeNi_2$. This calculation can be made more simple on the basis of a determination of the hypothetical lattice spacing of $CeNi_2$ with the cerium atoms either in the 4-valent state ($4f^0$) or in the 3-valent state ($4f^1$). If a_0 represents the lattice spacing of $CeNi_2$ (Ce-4 valent); a_1 the lattice spacing of $CeCo_2$ (0.7161 nm); b_1 the lattice spacing of $ZrCo_2$ (0.6960 nm) and b_0 the lattice spacing of $ZrNi_2$ (0.6916 nm), the following relation can be considered:

$$a_0/a_1 = b_0/b_1$$

which gives $a_0 = 0.7116$ nm. The lattice spacing of $CeNi_2$ in the 3-valent state can be obtained from the variation of the lattice spacing of the RNi_2 phases with the atomic diameter of the appropriate rare earth component [24], taking a diameter of 0.3669 nm for trivalent cerium [25]. Thus

$$CeNi_2\,(\text{Ce 3-valent}) \quad a = 0.7295\,\text{nm}$$

$$CeNi_2\,(\text{Ce 4-valent}) \quad a = 0.7116\,\text{nm}.$$

Assuming a linear relationship between the a-spacing of $CeNi_2$ with the cerium valency, then the measured value 0.7225 nm corresponds to a valency of 3.39 ± 0.01 for the cerium atoms,† i.e. to a configuration of 4f, 0.61, which gives for the $CeNi_2$ phase, an electron concentration of approximately 1.15 at the proposed limit of stability for the Laves structure. Thus the effective valency of 3.39 is the maximum allowable for the cerium atoms on the basis of phase stability, but a lower valency would increase the strain energy of the system and hence this particular electronic state could be the result of a compromise between the electronic and strain energy of the system.

Contrary to the present and previous work [5, 6], Olcese [26] has reported that cerium is in a 4-valent state in the $CeNi_2$ phase though such an observation is difficult to reconcile with (a) the lattice spacing of this phase, (ii) phase stability in the $Zr(Co_{1-x}Ni_x)_2$ system and (iii) the lattice spacing variations in the systems $Ce(Fe_{1-x}Ni_x)_2$ and $Ce(Co_{1-x}Ni_x)_2$. The evidence from X-ray photoelectron spectroscopy (XPS) studies is not conclusive [27–30] but Wallace *et al.* [15] interpreted

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*Actually, since $ZrNi_2$ is a non-stoichiometric compound, the use of the lattice parameter obtained from the non-stoichiometric $ZrNi_2$ should be considered as an approximation.

†This value for the effective valency of cerium in $CeNi_2$ is in reasonable agreement with the value of 3.5 obtained from a similar lattice spacing analysis and reported in [6].

some unusual features exhibited by $CeNi_2$ on the basis of a possible presence of a 4f character.

4. Conclusions

The variations of the room temperature magnetic susceptibility with composition in the $Zr(Co_{1-x}Ni_x)_2$ system shows a break in the linear behaviour of $x \simeq 0.76$ (51 at% Ni). The results have been interpreted, in terms of a decrease of the density of states at the Fermi level with the substitution of cobalt by nickel. The 51 at% Ni represents a critical composition for the ternary compound where the electron concentration reaches a critical value, thus limiting the stability of the cubic Laves phase. Therefore the compound based on $ZrNi_2$ can be regarded as a non-stoichiometric phase with an appropriate electron concentration.

In the $Ce(Co_{1-x}Ni_x)_2$ system, the unstable valency state of cerium has been employed to interpret the properties of this system, as follows: the lattice spacing behaviour is determined primarily by electronic factors; the increase in slope of the lattice spacings/composition variation at compositions given by $x > 0.33$ together with the fact that the magnetic susceptibility versus composition curve shows a distinct break in the slope at this composition, can be interpreted in terms of

(a) cerium atoms being in a valency state close to 4 from $0 \leqslant x \leqslant 0.33$

(b) an increase in the 4f population of cerium atoms at $x > 0.33$, accounts for the appearance of a χ_{4f} contribution to the total susceptibility which compensates for the expected fall in the density of states contribution due to the increasing nickel additions.

Calculations of the valency of cerium in $CeNi_2$ indicates that the electron concentration of this phase is at the limit for the formation of the Laves structure and this behaviour is regarded as a balance between electronic and strain energy factors.

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