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Valence state of cerium in the hexagonal CeM_5 compounds with the transition metals

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Résumé. — Nous avons étudié l'état de valence du cérium dans $CeCo_5$, $CeNi_5$, $CeCu_5$ et les composés pseudo-binaires $Ce(Ni_{1-x}Cu_x)_5$ à l'aide de mesures des paramètres de maille, des propriétés magnétiques et de l'étude de l'absorption des rayons X. Alors que les paramètres de maille de $CeCu_5$ correspondent à l'état de valence Ce^{3+} , les expériences d'absorption de rayons X montrent que dans $CeCo_5$ et $CeNi_5$, le cérium est dans le même état de valence, proche de $4+$, comme dans l'oxyde isolant CeO_2 . Les écarts à la stoechiométrie dans les composés RCO_5 ($R =$ terre rare) rendent compte des différences dans les anomalies du paramètre a des composés du Ce dans les séries RCO_5 et RNi_5 . Dans $Ce(Ni_{0.1}Cu_{0.9})_5$, Ce est dans l'état $3+$ et la variation thermique de sa susceptibilité est caractéristique des effets du champ cristallin sur l'ion Ce^{3+} . Au contraire, la susceptibilité de $CeNi_5$ est d'un ordre de grandeur inférieure et pratiquement isotrope; comme dans YNi_5 , elle provient essentiellement des électrons $3d$ du Ni, qui sont très proches de l'apparition du ferromagnétisme. Dans les composés $Ce(Ni_{1-x}Cu_x)_5$, le changement de valence du Ce est linéaire jusqu'à $x = 0,3$ et devient plus rapide pour les plus fortes concentrations. Nous discutons l'évolution de l'état de valence du Ce à partir de la structure de bande des différents composés, en particulier de la position du niveau de Fermi et de l'état $4f^1$.

Abstract. — The valence state of cerium in $CeCo_5$, $CeNi_5$, $CeCu_5$ and the pseudo-binary $Ce(Ni_{1-x}Cu_x)_5$ compounds has been studied by means of measurements of lattice parameters, magnetic properties and X-ray absorption. Whereas the lattice parameters of $CeCu_5$ correspond to a Ce^{3+} valence state, X-ray absorption experiments show that, in $CeCo_5$ and $CeNi_5$, Ce has the same valence state, close to $4+$, as in the insulator CeO_2 . Stoichiometry deviations in the RCO_5 compounds ($R =$ rare earth) can be correlated with the difference in the anomalies of the a lattice parameter of Ce compounds in the RCO_5 and RNi_5 series. In $Ce(Ni_{0.1}Cu_{0.9})_5$, Ce is in the $3+$ state and the thermal variation of the susceptibility is characteristic of crystal field effects in the Ce^{3+} ion. In contrast the susceptibility of $CeNi_5$ is one order of magnitude smaller and almost isotropic; as in YNi_5 , it arises mainly from the Ni $3d$ electrons which are close to the onset of ferromagnetism. In the $Ce(Ni_{1-x}Cu_x)_5$ compounds, the Ce valence state decreases linearly with x up to $x = 0.3$ and more rapidly for higher copper concentrations. The evolution of the Ce valence state is discussed in terms of the band structure of the different compounds, especially the relative position of the Fermi level and the $4f^1$ state.

1. **Introduction.** — The RM_5 compounds (with $R =$ rare earth and $M = Co, Ni, Cu$) crystallize in the hexagonal $CaCu_5$ -type structure (P6/mmm) where M atoms occupy two different sites : $2c(\frac{1}{3}, \frac{2}{3}, 0; \frac{2}{3}, \frac{1}{3}, 0)$ and $3g(\frac{1}{2}, 0, \frac{1}{2}; 0, \frac{1}{2}, \frac{1}{2}; \frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, while R atoms lie in

$1a(0, 0, 0)$. In such a close packed stacking of two different spherical atoms, the a cell parameter is directly related to the R and M atomic radii by $a = \sqrt{3}(r_R + r_M)$; the c parameter depends almost entirely on the M atomic radius :

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$$c = \sqrt{15 r_M(r_M - 2 r_R/15) - r_R^2}$$

In the RCu_5 series, the a parameter follows the lanthanide contraction : Ce is consequently trivalent in CeCu_5 . In CeNi_5 and CeCo_5 an abnormal reduction of the a parameter is observed which must be associated with a Ce valence higher than 3 [1]. In CeCo_5 a tetravalent state for Ce has been deduced from the comparison of its spontaneous magnetization ($5.5 \mu_B/\text{CeCo}_5$) with that of other ferromagnetic compounds : YCo_5 ($7.5 \mu_B$), LaCo_5 ($7.1 \mu_B$) and ThCo_5 ($4.8 \mu_B$) [2], in which thorium is tetravalent. A neutron diffraction study has confirmed that cerium is not magnetic in CeCo_5 [3]. The CeNi_5 compound is paramagnetic at any temperature. Its susceptibility shows a broad maximum around 100 K. Its thermal variation has been interpreted by Buschow *et al.* [4] as resulting from a progressive change from a $4+$ valence state of cerium at 0 K to an intermediate valence state at room temperature, due to thermal excitation to the $3+$ magnetic state. More recently, K. R. Bauchspiess *et al.* [5] have observed a similar double peaked edge of the L_{III} X-ray absorption of Ce in CeNi_5 and the insulator CeO_2 . Assuming that the absorption edge associated to an integral valence must always be single, they have deduced an intermediate valence close to 3.3 for these two compounds.

In the present study, the valence state of cerium in the CeM_5 compound is analysed from measurements of lattice parameters, magnetic properties and X-ray absorption. The Ce change of valence in the pseudobinary $\text{Ce}(\text{Ni}_{1-x}\text{Cu}_x)_5$ system is also studied.

The alloy constituents were 99.9% pure metals. The polycrystalline samples were melted by induction in a cold crucible. The CeNi_5 single crystal was prepared by the Czochralsky method.

2. Crystallographic properties. — The change of the lattice parameters with the Cu concentration x has been studied in the $\text{Ce}(\text{Ni}_{1-x}\text{Cu}_x)_5$ compounds and for comparison in the similar La, Pr and Nd alloys. For $0 \leq x \leq 0.9$ all the alloys were obtained in a single phase, and no miscibility gap was observed whatever the heat treatment employed. Figure 1 shows that the a and c parameters decrease as the Cu concentration x decreases from CeCu_5 to CeNi_5 . For the La, Pr and Nd alloys, the same monotonic variation is followed, as expected with rare earth $3+$ ions. In the Ce alloys, the same dependence is observed only down to $x = 0.8$. The Ce is then in the $3+$ state for $0.8 \leq x \leq 1$. Below $x = 0.8$, there occurs a deviation of the a parameter followed by a drastic decrease around $x = 0.4$. The deviation Δa from the $3+$ type variation (Fig. 1a, dashed line) is shown in figure 2a. A deviation of the c parameter is also found but it is much less pronounced. Around $x = 0.4$ the c parameter variation shows an inflection tangent with a very weak slope (Fig. 1b). As shown in the introduction, the c parameter is less dependent on the rare earth radius r_R than is the a parameter.

Such irregular variations of the lattice parameters

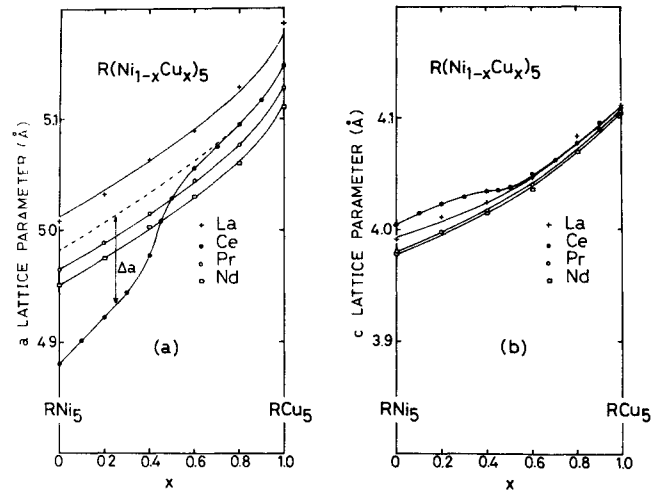


Fig. 1. — Lattice parameter variation versus the Cu concentration x in the $\text{R}(\text{Ni}_{1-x}\text{Cu}_x)_5$ compounds for $\text{R} = \text{La}, \text{Ce}, \text{Pr}$ and Nd . a) a lattice parameter. The dashed line corresponds to a variation of the Ce compound identical to the La, Pr and Nd ones. b) c lattice parameter. Values for $x = 1.0$ are taken from reference [1].

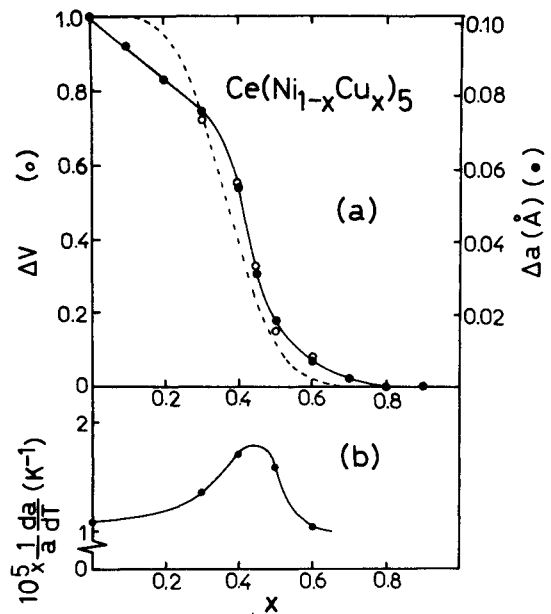


Fig. 2. — a) Deviation of the a lattice parameter Δa from a R^{3+} type variation (right hand scale, ●) and change of valence ΔV deduced from X-ray absorption experiments (left hand scale, ○) in the $\text{Ce}(\text{Ni}_{1-x}\text{Cu}_x)_5$ compounds versus the Cu concentration x . The dashed line represents the best fit in a Jaccarino-Walker [17] type model. b) Dilatation coefficient α_a between 150 and 300 K in the $\text{Ce}(\text{Ni}_{1-x}\text{Cu}_x)_5$ compounds.

could be attributed to a preferential order of the Cu and Ni atoms on the $2c$ and $3g$ sites. This would be detected by neutron diffraction experiments because of the difference in the Cu and Ni scattering lengths ($b_{\text{Cu}} = 0.76 \times 10^{-12} \text{ cm}$ and $b_{\text{Ni}} = 1.03 \times 10^{-12} \text{ cm}$). Two alloys, with Cu concentrations on both sides of the large increase of the a parameter were studied : $\text{Ce}(\text{Ni}_{0.7}\text{Cu}_{0.3})_5$ ($x = 0.3$) and $\text{Ce}(\text{Ni}_{0.4}\text{Cu}_{0.6})_5$ ($x = 0.6$).

To enhance the probability of ordering, samples were annealed for 3 days at 700 °C and then cooled down to room temperature at a rate of 0.5°/min.

The occupancies x_{2c} and x_{3g} of the 2 sites were obtained by refining the mean scattering lengths of the M atoms $b_{M_{2c}}$ and $b_{M_{3g}}$:

$$b_{M_{2c}} = x_{2c} b_{Cu} + (1 - x_{2c}) b_{Ni}$$

and

$$b_{M_{3g}} = x_{3g} b_{Cu} + (1 - x_{3g}) b_{Ni}$$

x_{2c} and x_{3g} are correlated to each other through the total Cu concentration x by the relation

$$2 x_{2c} + 3 x_{3g} = 5 x .$$

The best agreements were found for the following values :

for $x = 0.3$:

$$x_{2c} = 0.33 \pm 0.03 \text{ implying } x_{3g} = 0.28 \pm 0.02 ,$$

for $x = 0.6$:

$$x_{2c} = 0.65 \pm 0.03 \text{ implying } x_{3g} = 0.57 \pm 0.02 .$$

The calculated intensities I_c are compared to the observed ones I_o on table I. The reliability factors $R = \Sigma |I_o - I_c| / \Sigma I_o$ are 3.2 % for $x = 0.3$ and 2.3 % for $x = 0.6$. For both compounds the Cu atoms are almost equally distributed on the 2 sites and the irregular variations of the lattice parameters cannot be associated with a preferential order of Ni and Cu atoms on the 2c and 3g sites; the large increase of the a parameter has to be attributed to an increase of the Ce atomic radius.

In order to check the interpretation of Buschow *et al.* [4] which involves a thermal change of valence of Ce in CeNi₅, we have undertaken a study of the thermal variation of the lattice parameters of CeNi₅, as well as those of LaNi₅ and several Ce(Ni_{1-x}Cu_x)₅ alloys, around the drastic change of a ($x = 0.3, 0.4, 0.5, 0.6$) for comparison. The measurements were obtained by X-ray diffraction with Cr radiation ($\lambda = 2.28962 \text{ \AA}$)

Table I. — Neutron diffraction experiment : comparison of the observed (I_o) and calculated (I_c) intensities in Ce(Ni_{0.7}Cu_{0.3})₅ and Ce(Ni_{0.4}Cu_{0.6})₅ at room temperature.

Ce(Ni _{0.7} Cu _{0.3}) ₅					Ce(Ni _{0.4} Cu _{0.6}) ₅				
hkl	θ	I_o	I_c		θ	I_o	I_c		
100	10.9	300	310		10.7	243	274		
001	11.6	48	40		11.5	30	34		
101	16.0	30	36		15.8	38	41		
110	19.1	278	284		18.7	275	280		
200	22.2	} 2 459	813	} 2 355	21.7	} 2 355	808	} 2 300	
111	22.6		1 542		22.2		1 492		
002	23.7	3 777	3 801		23.6	3 629	3 646		
201	25.3	1 569	1 538		24.8	1 452	1 422		
102	26.4	249	280		26.1	272	248		
210	30.0	262	270		29.3	215	241		
112	31.2	217	246		30.8	255	243		
211	32.6	} 905	28	} 972	31.9	} 954	33	} 973	
202	33.5		710		33.0		707		
300	34.5		235		33.7		233		

$$R = 3.2 \%$$

$$R = 2.3 \%$$

from 4.2 K to room temperature. For all the compounds studied, the thermal dilatation along the *c*-axis is almost the same, the dilatation coefficient $\alpha_c = \Delta c/c \Delta T$ between 150 and 300 K being

$$(1.08 \pm 0.05) \cdot 10^{-5} \text{ K}^{-1}.$$

The thermal variation of the *a* parameter of CeNi₅ is identical to that of LaNi₅ (Fig. 3). There is therefore no change of the Ce valence in CeNi₅ as the temperature increases from 4.2 K to room temperature. In the Ce pseudo-binary alloys the dilatation coefficient $\alpha_a = \Delta a/a \Delta T$ measured between 150 and 300 K shows a maximum around *x* = 0.4 and 0.5, these being the Cu concentrations for which the *a* parameter varies drastically (Fig. 2*b*). These latter compounds might present a thermal change of the Ce valence.

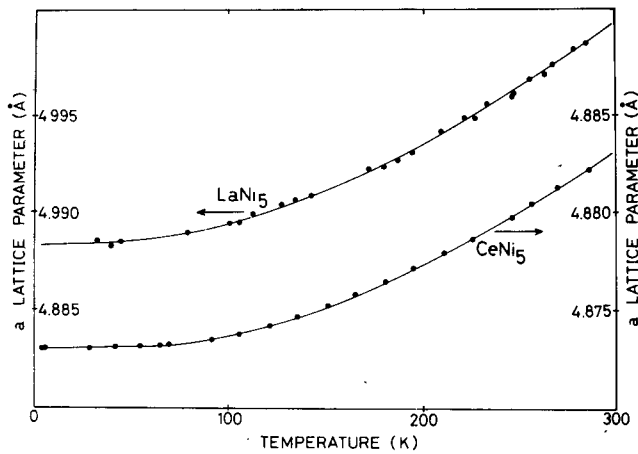


Fig. 3. — Thermal expansion of the *a* parameter in CeNi₅ (right hand scale) and LaNi₅ (left hand scale).

3. Resistivity and magnetic properties. — The resistivity and the magnetic susceptibility of CeNi₅ were studied on a single crystal along the *a* and *c* directions from 4.2 K to room temperature. The thermal dependence of the resistivity is monotonic but strongly anisotropic because of the uniaxial character of the crystallographic structure (Fig. 4). At very low temperatures it has a BT^2 dependence, the *B* coefficient value being $7 \times 10^{-10} \Omega \text{ cm K}^{-2}$ along *c* and $11 \times 10^{-10} \Omega \text{ cm K}^{-2}$ along *a*, and the residual resistivities are 1.4 and $3.2 \times 10^{-6} \Omega \text{ cm}$ respectively.

The CeNi₅ magnetization was measured at 4.2 K as a function of the magnetic field applied parallel to the *c*-axis (Fig. 5, insert) : its variation in fields larger than 50 kOe is linear, the magnetization of the impurities being almost saturated. The value of the CeNi₅ intrinsic susceptibility at 4.2 K is given by the slope of this straight line : $(30 \pm 2) \cdot 10^{-4} \text{ e.m.u./mole}$. The thermal dependence of the CeNi₅ susceptibility was measured on a translation balance in order to get a more accurate variation (Fig. 5). However, at very low temperatures, a contribution due to the magnetic

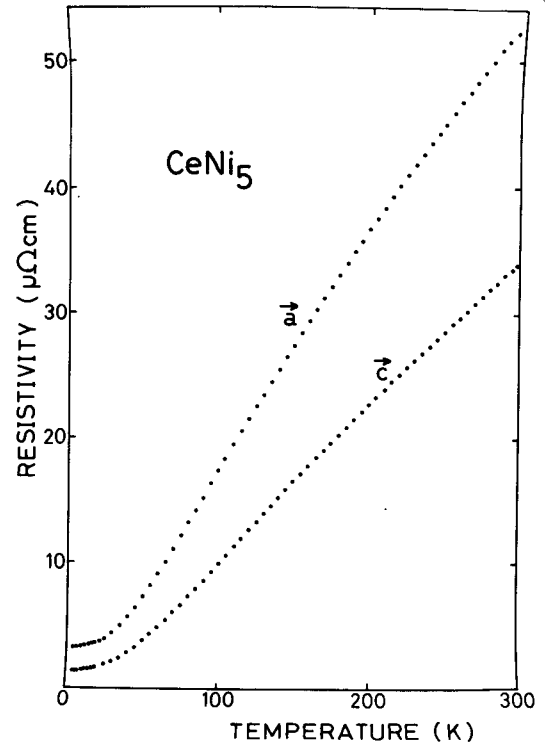


Fig. 4. — Thermal variation of the resistivity of CeNi₅ measured along the *a* and *c* directions.

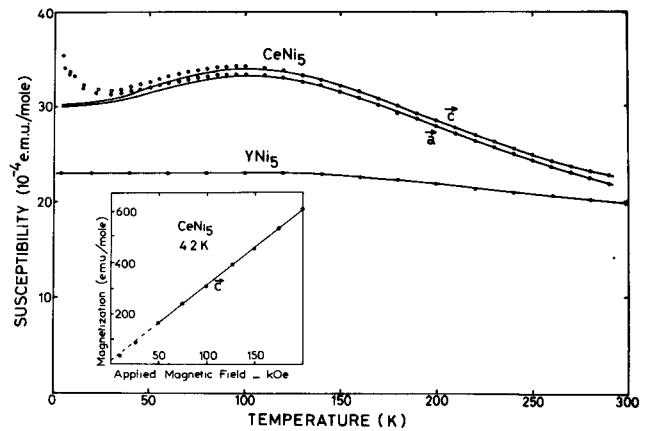


Fig. 5. — Thermal variations of the susceptibilities of YNi₅ [9] and of CeNi₅ measured along the *a* (●) and *c* (○) directions. The continuous lines are the corrected intrinsic susceptibilities. Insert : field dependence of the CeNi₅ magnetization at 4.2 K along the *c* direction.

impurities adds to the CeNi₅ intrinsic susceptibility, leading especially to an increase of the measured susceptibility below 30 K. The CeNi₅ intrinsic susceptibility χ_{int} was then obtained by correcting this susceptibility measured on the translation balance χ_{meas} as described by Béal-Monod and Lawrence [6] for the CeIn_{3-x}Sn_x compounds : $\chi_{\text{int}} = \chi_{\text{meas}} - C_{\text{imp}}/T$. Assuming that the thermal variation of χ_{int} follows between 4.2 K and 50 K the law [6] :

$$\chi_{\text{int}}(T) = \chi(0) + AT^2,$$

the parameters $\chi(0)$, A and C_{imp} were obtained from least square fits. Their values are

$$\chi(0) = 29.8 \times 10^{-4} \text{ e.m.u./mole,}$$

$$A = 7 \times 10^{-8} \text{ e.m.u. K}^{-2}/\text{mole}$$

and $C_{\text{imp}} = 30 \times 10^{-4} \text{ e.m.u. K/mole}$

for the field applied along **a** and

$$\chi(0) = 30.3 \times 10^{-4} \text{ e.m.u./mole,}$$

$$A = 8 \times 10^{-8} \text{ e.m.u. K}^{-2}/\text{mole}$$

and $C_{\text{imp}} = 25 \times 10^{-4} \text{ e.m.u. K/mole}$.

for the field applied along **c**. The thermal dependence of the intrinsic susceptibilities along **a** and **c** are compared in figure 5. The anisotropy is very weak. As previously determined by Buschow *et al.* [4] on a polycrystalline sample, the CeNi₅ susceptibility shows a broad maximum around 100 K, similar to those observed in YCo₂ [7] or LuCo₂ [8]. Moreover, at any temperature, the value of the CeNi₅ susceptibility is close to those of LaNi₅ and YNi₅ (18 and $20 \times 10^{-4} \text{ e.m.u./mole}$ respectively, at 300 K). In figure 5, we have compared the thermal variation of CeNi₅ to that of YNi₅ which had been previously measured on a single crystal [9]. The physical properties of the Y-Ni and La-Ni compounds in which the Ni is close to the onset of magnetism are quite similar and very sensitive to the presence of impurities such as neighbouring phases. The Y compounds are easier to prepare as single crystals and, for this reason, their properties are better known [10].

The Ce(Ni_{0.1}Cu_{0.9})₅ susceptibility was measured on a polycrystalline sample. Its value at 20 K is $27 \times 10^{-3} \text{ e.m.u./mole}$ which is one order of magnitude larger than in CeNi₅. The reciprocal susceptibility (Fig. 6) follows a Curie-Weiss type law above 50 K with a slope corresponding to an effective moment of $2.56 \mu_B$ which is very close to the expected value for Ce³⁺ ($2.54 \mu_B$). Below 50 K, the observed susceptibility

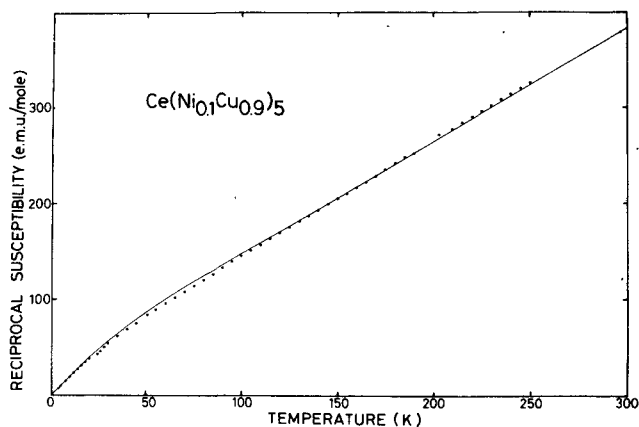


Fig. 6. — Thermal variation of the reciprocal susceptibility of Ce(Ni_{0.1}Cu_{0.9})₅: ● experimental point, — calculated curve for the parameters given in the text.

is characteristic of the effects of a uniaxial crystal field on a 4f ion, which tend to reduce the magnetic moment. A good agreement between the observed and the calculated variation is found for negligible magnetic exchange interactions between Ce atoms and with the following values of the crystal electric field parameters: $B_2^0 = 20 \text{ K}$, $B_4^0 = 0.5 \text{ K}$. There are no 6th order terms associated with Ce³⁺. These values are in agreement with those deduced from various RNi₅ compounds [11] by a scaling law ($B_2^0 = 15.5 \text{ K}$, $B_4^0 = -0.38 \text{ K}$). They lead to a $\pm 1/2$ ground state for Ce in the compound studied.

4. X-ray absorption study. — The X-ray absorption measurements were performed on a (220) silicon monochromator, using the synchrotron radiation of D.C.I. at L.U.R.E. (Orsay, France). Intensities were measured before and after the sample using conventional ionization chambers. The powdered samples were held on a sticky tape. Several sample thicknesses were studied in order to test for the influence of beam harmonics, which turned out to be negligible. Figure 7 shows the structure of the Ce L_{III} absorption edges

$$(\text{Ce } 2p \ 3/2 \rightarrow E_F, \Delta E \sim 5.7 \text{ keV})$$

in Ce(Ni_{1-x}Cu_x)₅ for $x = 0.8, 0.6, 0.5, 0.4, 0.3$ and 0 as well as in CeCo₅ and the insulator CeO₂. The difference between the absorption curve before the edge, and the mean absorption averaged over the EXAFS oscillations after the edge is normalized to 1. As shown in section 2, the Ce ion in Ce(Ni_{0.2}Cu_{0.8})₅ is in the normal trivalent state. The L_{III} edge of Ce in this compound presents a strong peak, which is a few electron volts wide. This peak is in fact a general feature for rare earth atoms in a trivalent state and is largely due to transitions into empty 5d states. A double absorption edge is observed in CeO₂ which is a good insulator. To preserve electro-neutrality, the cerium must be in the Ce⁴⁺ state in this ionic oxide. Since our sample was checked to be perfectly pure by magnetic and crystallographic analysis, this double peaked edge is characteristic of Ce⁴⁺ and must be related to two different final states, the additional one corresponding to a change in the 4f occupancy [12]. The CeCo₅ and CeNi₅ spectra are similar to that of CeO₂. Ce is therefore very close to a tetravalent state in these two intermetallic compounds. Their absorption edges lie at lower energy than that of CeO₂ because their Fermi energies lie below the 5d ionic level. For Cu concentrations ranging from 0.8 to 0.3 the shape of the absorption edge changes gradually from that characteristic of the trivalent state (A) to that characteristic of the almost tetravalent state (B). Analysis of these spectra by fractional superposition of (A) and (B) spectra gives the valence change ΔV as a function of the concentration x . This variation is compared to the a variation in figure 2a. The two curves are quite superposed. The anomalous variation of the a lattice parameter is thus due to a change of the Ce valence

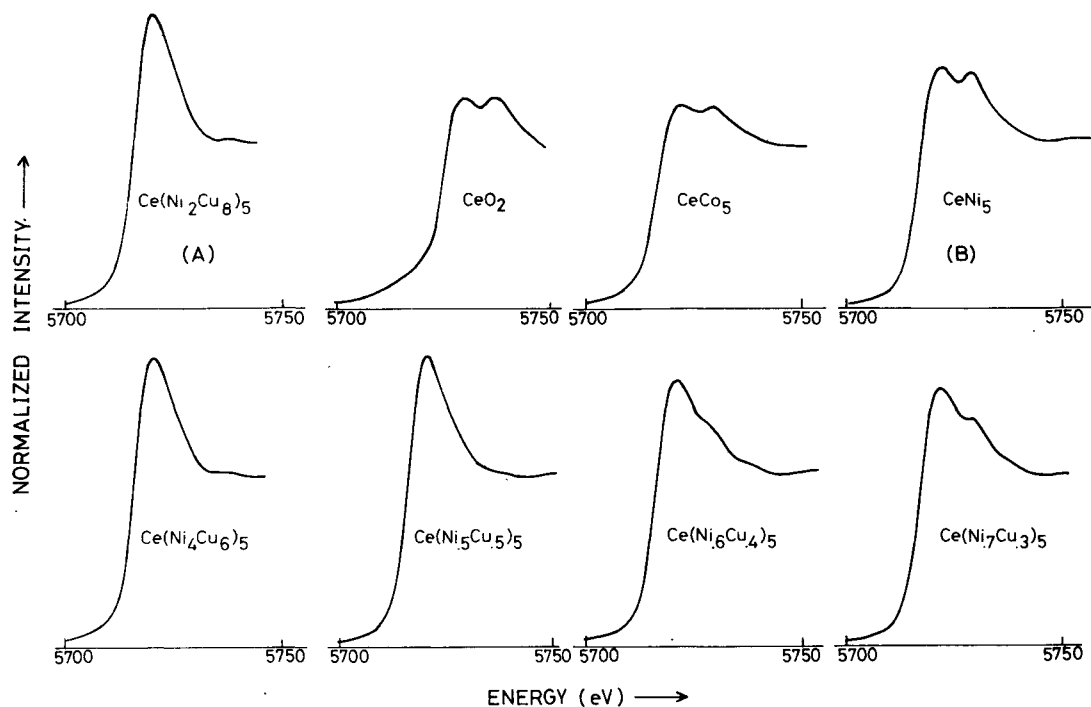


Fig. 7. — L_{III} absorption edges for Ce in $CeNi_5$, $CeCo_5$, CeO_2 and various $Ce(Ni_{1-x}Cu_x)_5$ alloys at room temperature.

from almost $4+$ to $3+$ with increasing Cu concentration.

5. Discussion. — The two $CeNi_5$ and $CeCo_5$ compounds exhibit the same L_{III} X-ray absorption edges as in CeO_2 , implying that in these two compounds Ce is very close to a tetravalent state. This conclusion, which is different from that of Bauchspiess *et al.* [5] is based on a different interpretation of the double peaked edge in CeO_2 . In this ionic insulator, an intermediate valence of 3.3 of Ce does not preserve electroneutrality, while the double peak observed can be due to two different final states after the X-ray absorption process [12]. Moreover, our conclusion is consistent with the other experimental results presented in this paper.

The a lattice parameter variation inside the series RCu_5 , RCO_5 and RNi_5 [1] is reported in figure 8. The lattice anomaly is smaller in $CeNi_5$ (0.105 \AA) than in $CeCo_5$ (0.145 \AA). As this difference does not result from different valence states, it can be explained by slight changes in their stoichiometries. RNi_5 compounds are generally stoichiometric while for the RCO_5 compounds with small radii rare earths, an increase of Co concentration stabilizes the phase : for instance the composition of the alloy with Er reaches $ErCo_6$ [13, 14]. The excess of Co is caused by Co dumb-bells parallel to c replacing rare earth atoms : this involves an increase of the c parameter and simultaneously a decrease of the a parameter. The thin line on figure 8 represents the a parameter variation in RCO_5 compounds without any change in stoichiometry. It was obtained from the a parameter variation in the RNi_5

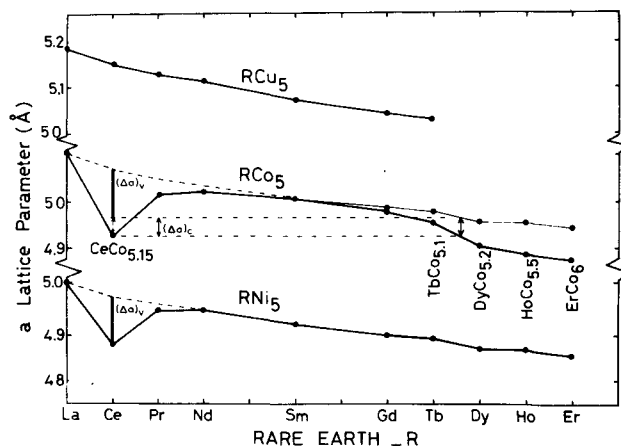


Fig. 8. — a lattice parameters in the series RCu_5 , RCO_5 and RNi_5 . The dashed line corresponds to the RCu_5 type variation. The thin line is parallel to the RNi_5 variation.

compounds. The parameter anomaly in $CeCo_5$ results from combined effects : the anomaly $(\Delta a)_v (= 0.105 \text{ \AA})$ is due to the Ce volume reduction in the tetravalent state ; it involves an increase of the Co concentration and then an additional decrease $(\Delta a)_c (= 0.040 \text{ \AA})$ of the a parameter. The composition of the cerium-cobalt compound thus deduced is $CeCo_{5.15}$. According to the relation $a = \sqrt{3}(r_{Ce} + r_M)$, the relative variation of the Ce atomic radius $\Delta r_{Ce}/r_{Ce}$ associated with the a parameter reduction due to the change of valence $(\Delta a)_v$ would be 5%. In fact, this relative variation reaches 9% in Ce metal [15], or in a Ce ion [16]. This difference can be attributed to the modification of the band structure. In $CeCo_5$ or $CeNi_5$, due to the almost

tetravalent state of cerium, more electrons are transferred to the 3d band, and the reduction of the Ce-M distance (that is the a reduction) is less important due to hybridization effects. In conclusion, in order to analyse a valence change from the variation of the lattice parameters, it is necessary to take account, not only of the volume dependence of the ions, but also of the stoichiometry changes which generally occur and of the modification of the band structure, in the case of intermetallic compounds.

The valence state of Ce in the various compounds studied depends in fact on the possibility of transferring 5d electrons towards the 3d band. In Co and Ni, the 3d band is unfilled; because of the difference in electronegativity between these elements and the rare earths, 5d electrons are transferred to the 3d band, lowering the Fermi level E_F of the compound compared to the Fermi level of the rare earth metal. If the $4f^1$ level is higher than E_F , the Ce becomes tetravalent. With Cu, the 3d band is filled up and no transfer is then possible: the Ce remains trivalent.

The change from the almost 4+ to the 3+ valence state is observed in the $Ce(Ni_{1-x}Cu_x)_5$ compounds with increasing concentration x (Fig. 2a). The Ce valence state decreases linearly with x up to $x = 0.3$ and more rapidly for higher copper concentrations. A drastic change of valence related to a critical number of near neighbour Cu atoms cannot account for such a dependence: as a matter of fact, the best fit to the experimental variation (Fig. 2a, dashed line) calculated within a statistical model of the Jaccarino-Walker type [17] corresponds to a critical number of 7 Cu atoms among the 18 Cu or Ni atoms neighbouring one Ce atom. The agreement is very poor for the low copper concentrations. In fact, the experimental curve shows two processes: the regular decrease of the valence as x increases from 0 to $x = 0.3$ could be interpreted by the progressive filling of a $4f^1$ virtual bound state. In $CeNi_5$ this bound state is almost empty. The filling occurs as the Fermi level rises because of the decreased transfer of electrons towards the 3d band with increasing x . For concentrations above $x = 0.3$, the existence of a critical concentration and of associated neighbouring effects could account for the drastic decrease of the Ce valence. In fact, theoretical calculations in the Anderson model [18] show the existence of such a critical value of x .

Moreover, it can be noted that the thermal dilatation coefficient α_a presents a maximum (Fig. 2b) for x values corresponding to the steepest part of the curve $\Delta V(x)$ ($0.4 < x < 0.5$). However, for these compounds, the thermal change of valence between 150 and 300 K, deduced from the ΔV variation versus Δa (Fig. 2a) is $\Delta V = 0.05$ only.

The magnetic properties can also be well explained taking into account the valence states determined above. It has been shown that the thermal variation of the susceptibility of $Ce(Ni_{0.1}Cu_{0.9})_5$ is characteristic of the effects of a uniaxial crystalline field on the Ce^{3+}

ion. In such a case, the susceptibility is anisotropic, as are those of the other RNi_5 compounds [11] ($R \neq Ce$ or Gd). In $CeNi_5$, the susceptibility exhibits a negligible anisotropy, which cannot originate from 4f electrons. Moreover, its value is comparable to those of $LaNi_5$ and YNi_5 . In fact, $CeNi_5$, like $LaNi_5$ and YNi_5 , is an enhanced Pauli paramagnet close to the Stoner criterion, as confirmed by the BT^2 low temperature dependence of its resistivity. In the (Y-Ni) system, a resurgence of ferromagnetism is observed for the compounds with a Y concentration between YNi_5 and YNi_2 . This phenomenon can be explained by an increase of the 3d-4d hybridization as the Y concentration increases, involving an increase of the density of states at the Fermi level [19]. In addition, the greater number of conduction electrons in Ce, corresponding to its almost tetravalent state, implies a greater 3d-5d hybridization in $CeNi_5$ than in YNi_5 . Therefore the density of states at the Fermi level and hence the susceptibility are larger in $CeNi_5$ than in YNi_5 . The band structures of the two compounds deduced from the calculations of Cyrot and Lavagna [20] are schematically drawn on figure 9. They

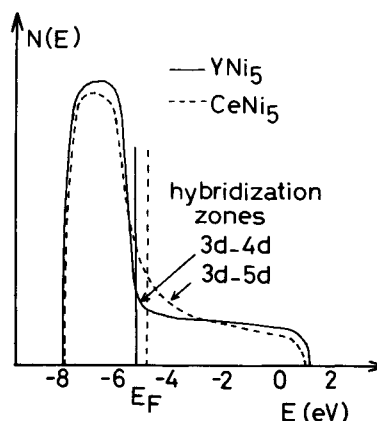


Fig. 9. — Scheme of the d density of state curves in YNi_5 (—) and $CeNi_5$ (---).

allow an explanation of the thermal variation of the susceptibilities. As shown by Wohlfarth and Rhodes [21] for enhanced paramagnetism, and by Béal-Monod and Lawrence [6] in the paramagnon picture, the maximum observed in $CeNi_5$ could result from the Fermi level lying in a zone of the density of states with a positive curvature. At low temperature ($T < 50$ K) the $CeNi_5$ intrinsic susceptibility follows the law characteristic of a nearly magnetic fermion system [6]: $\chi(T) = \chi(0) + AT^2$, where A is positive. In YNi_5 , the Fermi level does not lie in a zone with a positive strong curvature. Consequently the susceptibility decreases slightly with increasing temperature. A polarized neutron study [22] has actually confirmed that the dominant part of the $CeNi_5$ susceptibility originates from a 3d magnetism associated with the Ni atoms, as in YNi_5 [23].

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