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Valence state of cerium in the hexagonal CeM₅ compounds with the transition metals

D. Gignoux, F. Givord, R. Lemaire
Laboratoire Louis-Néel (*), C.N.R.S., 166X, 38042 Grenoble Cedex, France

H. Launois
C.N.E.T., 106, rue de Paris, 92220 Bagneux, France

and F. Sayetat
Laboratoire de Cristallographie (*), C.N.R.S., 166X, 38042 Grenoble Cedex, France

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Résumé. — Nous avons étudié l'état de valence du cérium dans CeCo₅, CeNi₅, CeCu₅ et les composés pseudo-binaires Ce(Ni₁₋ₓCux)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 CeCu₅ correspondent à l'état de valence Ce³⁺, les expériences d'absorption de rayons X montrent que dans CeCo₅ et CeNi₅, le cérium est dans le même état de valence, proche de 4 +, comme dans l'oxyde isolant CeO₂. Les écarts à la stoechiométrie dans les composés RCo₅ (R = terre rare) rendent compte des différences dans les anomalies du paramètre a des composés du Ce dans les séries RCo₅ et RNi₅. Dans Ce(Ni₀,₁Cu₀,₉)₅, Ce est dans l'état 3 + et la variation thermique de sa susceptibilité est caractéristique des effets du champ cristallin sur l'ion Ce³⁺. Au contraire, la susceptibilité de CeNi₅ est d'un ordre de grandeur inférieure et pratiquement isotrope ; comme dans YNi₅, elle provient essentiellement des électrons 3d du Ni, qui sont très proches de l'apparition du ferromagnétisme. Dans les composés Ce(Ni₁₋ₓCux)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.

Abstract. — The valence state of cerium in CeCo₅, CeNi₅, CeCu₅ and the pseudo-binary Ce(Ni₁₋ₓCux)₅ compounds has been studied by means of measurements of lattice parameters, magnetic properties and X-ray absorption. Whereas the lattice parameters of CeCu₅ correspond to a Ce³⁺ valence state, X-ray absorption experiments show that, in CeCo₅ and CeNi₅, Ce has the same valence state, close to 4 +, as in the insulator CeO₂. Stoichiometry deviations in the RCo₅ compounds (R = rare earth) can be correlated with the difference in the anomalies of the a parameter of Ce compounds in the RCo₅ and RNi₅ series. In Ce(Ni₀,₁Cu₀,₉)₅, Ce is in the 3 + state and the thermal variation of the susceptibility is characteristic of crystal field effects in the Ce³⁺ ion. In contrast the susceptibility of CeNi₅ is one order of magnitude smaller and almost isotropic; as in YNi₅, it arises mainly from the Ni 3d electrons which are close to the onset of ferromagnetism. In the Ce(Ni₁₋ₓCux)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 4f⁴ state.

1. Introduction. — The RM₅ compounds (with R = rare earth and M = Co, Ni, Cu) crystallize in the hexagonal CaCu₅-type structure (P6/mmm) where M atoms occupy two different sites : 2a(1, 1, 0), 3g(0, 1, 1), and 3g(0, 1, 0, 1, 1, 1; 1, 1, 0; 1, 1, 1) 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

\[ a = \sqrt{3}(r_R + r_M) \]

and the c parameter depends almost entirely on the M atomic radius :

\[ c = \sqrt{15} r_M(r_M - 2 r_R/15) - r_R^2. \]

(*) Laboratoires propres du C.N.R.S., associés à l'Université Scientifique et Médicale de Grenoble.
In the RCu₅ series, the a parameter follows the lanthanide contraction: Ce is consequently trivalent in CeCu₅. In CeNi₅ and CeCo₅, an abnormal reduction of the a parameter is observed which must be associated with a Ce valence higher than 3 [1]. In CeCo₅, a tetravalent state for Ce has been deduced from the comparison of its spontaneous magnetization (5.5 µB/CeCo₅) with that of other ferromagnetic compounds: YCo₅ (7.5 µB), LaCo₅ (7.1 µB) and ThCo₅ (4.8 µB) [2], in which thorium is tetravalent. A neutron diffraction study has confirmed that cerium is not magnetic in CeCo₅ [3]. The CeNi₅ 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 L₃₃ X-ray absorption of Ce in CeNi₅ and the insulator CeO₂. 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 CeM₅ compound is analysed from measurements of lattice parameters, magnetic properties and X-ray absorption. The Ce change of valence in the pseudo-binary Ce(Ni₁₋ₓCuₓ)₅ system is also studied.

Two alloys, with Cu concentrations on both sides of the large increase of the a parameter were studied:

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In the present study, the valence state of cerium in the CeM₅ compound is analysed from measurements of lattice parameters, magnetic properties and X-ray absorption. The Ce change of valence in the pseudo-binary Ce(Ni₁₋ₓCuₓ)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 CeNi₅ 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 Ce(Ni₁₋ₓCuₓ)₅ compounds and for comparison in the similar La, Pr and Nd alloys. For 0 ≤ x ≤ 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 CeCu₅ to CeNi₅. 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 ≤ x ≤ 1. Below x = 0.8, there occurs a deviation of the a parameter followed by a drastic decrease around x = 0.4. The deviation ∆a 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 rₑ than is the a parameter.

Such irregular variations of the lattice parameters 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 (bₑCu = 0.76 × 10⁻¹² cm and bₑNi = 1.03 × 10⁻¹² cm). Two alloys, with Cu concentrations on both sides of the large increase of the a parameter were studied: Ce(Ni₀₋ₓCuₓ)₅ (x = 0.3) and Ce(Ni₀₋ₓCuₓ)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°C/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 \( R = \frac{\sum |I_o - I_c|}{\sum I_o} \) 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 CeNi\( _x \), we have undertaken a study of the thermal variation of the lattice parameters of CeNi\( _x \) as well as those of LaNi\( _x \) 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 (\( \lambda = 2.28962 \) Å).

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.

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<th>( I_o )</th>
<th>( I_c )</th>
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</table>

\( R = 3.2\% \)

\( R = 2.3\% \)
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

\[
(1.08 \pm 0.05) \times 10^{-5} \text{ K}^{-1}.
\]

The thermal variation of the \( a \) parameter of CeNi\(_5\) is identical to that of LaNi\(_5\) (Fig. 3). There is therefore no change of the Ce valence in CeNi\(_5\) 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. 2b). These latter compounds might present a thermal change of the Ce valence.

Fig. 3. — Thermal expansion of the \( a \) parameter in CeNi\(_5\) (right hand scale) and LaNi\(_5\) (left hand scale).

3. Resistivity and magnetic properties. — The resistivity and the magnetic susceptibility of CeNi\(_5\) 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 \( 7 \times 10^{-10} \) \( \Omega \) cm K\(^{-2} \) along \( c \) and \( 11 \times 10^{-10} \) \( \Omega \) cm K\(^{-2} \) along \( a \), and the residual resistivities are 1.4 and \( 3.2 \times 10^{-6} \) \( \Omega \) cm respectively.

The CeNi\(_5\) 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 CeNi\(_5\) intrinsic susceptibility at 4.2 K is given by the slope of this straight line: \((30 \pm 2) \times 10^{-4} \text{ e.m.u./mole.} \)

The thermal dependence of the CeNi\(_5\) 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 impurities adds to the CeNi\(_5\) intrinsic susceptibility, leading especially to an increase of the measured susceptibility below 30 K. The CeNi\(_5\) intrinsic susceptibility \( \chi_{\text{int}} \) was then obtained by correcting this susceptibility measured on the translation balance \( \chi_{\text{meas}} \) as described by Béal-Monod and Lawrence [6] for the CeNi\(_{3-x}\)Sn\(_x\) compounds: \( \chi_{\text{int}} = \chi_{\text{meas}} - C_{\text{imp}} / T \).

Assuming that the thermal variation of \( \chi_{\text{int}} \) 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 $C_{\text{imp}}$ 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 CeNi$_5$ susceptibility shows a broad maximum around 100 K, similar to those observed in YCo$_2$ [7] or LuCo$_2$ [8]. Moreover, at any temperature, the value of the CeNi$_5$ susceptibility is close to those of LaNi$_5$ and YNi$_5$ (18 and $20 \times 10^{-4}$ e.m.u/mole respectively, at 300 K). In figure 5, we have compared the thermal variation of CeNi$_5$ to that of YNi$_5$ 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$_{1-x}$Cu$_x$)$_5$ susceptibility was measured on a polycrystalline sample. Its value at 20 K is $27 \times 10^{-4}$ e.m.u/mole which is one order of magnitude larger than in CeNi$_5$. The reciprocal susceptibility 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 Ce$^{3+}$ ($2.54 \mu_B$). Below 50 K, the observed susceptibility 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: $B_2^0 = 20$ K, $B_4^0 = 0.5$ K. There are no 6th order terms associated with Ce$^{3+}$. These values are in agreement with those deduced from various RNi$_5$ compounds [11] by a scaling law ($B_2^0 = 15.5$ K, $B_4^0 = -0.38$ 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$_{\text{III}}$ 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 CeCo$_2$ and the insulator CeO$_2$. 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$_{1.2}$Cu$_{0.8}$)$_5$ is in the normal trivalent state. The L$_{\text{III}}$ 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 CeO$_2$ which is a good insulator. To preserve electro-neutrality, the cerium must be in the Ce$^{4+}$ 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 Ce$^{4+}$ and must be related to two different final states, the additional one corresponding to a change in the 4f occupancy [12]. The CeCo$_2$ and CeNi$_5$ spectra are similar to that of CeO$_2$. Ce is therefore very close to a tetravalent state in these two intermetallic compounds. Their absorption edges lie at lower energy than that of CeO$_2$ 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 $\Delta V$ as a function of the concentration $x$. This variation is compared to the $\alpha$ variation in figure 2a. The two curves are quite superposed. The anomalous variation of the $\alpha$ 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 Å) than in CeCo$_5$ (0.145 Å). 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$_5$ compounds. The parameter anomaly in CeCo$_5$ results from combined effects: the anomaly ($\Delta a$)$_c$ (0.105 Å) is due to the Ce volume reduction in the tetravalent state; it involves an increase of the Co concentration and then an additional decrease ($\Delta a$)$_a$ (0.040 Å) of the $a$ parameter. The composition of the cerium-cobalt compound thus deduced is CeCo$_5$. According to the relation $a = \sqrt{3(r_{ce} + r_{co})}$, 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 ($\Delta a$)$_a$ 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 $\alpha$ 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 $\Delta V$ variation versus $\Delta a$ (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$^{5+}$ 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$_3$ and YNi$_3$. In fact, CeNi$_5$, like LaNi$_3$ and YNi$_3$, 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$_3$ 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$_3$. Therefore the density of states at the Fermi level and hence the susceptibility are larger in CeNi$_5$ than in YNi$_3$. The band structures of the two compounds deduced from the calculations of Cyrot and Lavagna [20] are schematically drawn on figure 9. They 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$_3$, 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$_3$ [23].
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