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THERMAL DEPENDENCE OF THE SUSCEPTIBILITY DENSITIES IN CeNi\textsubscript{5}

D. Gignoux, F. Givord, R. Lemaire and F. Tasset

Laboratoire Louis Néel, C.N.R.S., 166 X, 38042 Grenoble Cedex, France
*Institut Laue-Langevin, 156 X, 38042 Grenoble Cedex, France

Résumé. - Afin de préciser l'origine du maximum à 100 K de la variation thermique de la susceptibilité du composé paramagnétique CeNi\textsubscript{5} nous avons effectué une étude par neutrons polarisés à différentes températures et dans un champ magnétique de 46,2 kOe. La projection de l'aimantation induite montre de fortes densités positives localisées sur les sites de Ni et une faible contribution sur les sites de Ce. Le maximum de la susceptibilité macroscopique correspond à un maximum de la susceptibilité sur les 5 atomes de Ni. A cette contribution 3d est également superposée à 100 K une forte polarisation antiparallèle, plus diffuse et non uniforme.

Abstract. - In order to evidence the origin of the maximum at 100 K in the thermal variation of the susceptibility of the paramagnet CeNi\textsubscript{5}, a polarized neutron study has been performed at various temperatures and in a magnetic field of 46.2 kOe. The projection of the induced magnetization evidences strong positive densities localized on the Ni sites and a weak contribution on the Ce sites. The maximum of the bulk susceptibility corresponds to a maximum of the susceptibility of the 5 Ni atoms. To this 3d-type contribution is also superposed at 100 K a strong antiparallel polarization, more diffuse and non uniform.

Introduction

The CeNi\textsubscript{5} compound, which crystallizes in the hexagonal CaCu\textsubscript{5}-type structure, is paramagnetic at any temperature, the thermal variation of its susceptibility showing a broad maximum around 100 K (figure 1). Two different interpretations have been proposed for this maximum. One\(^1\) in which it is considered that the maximum results 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. In the second one\(^2\), Ce is considered to be non magnetic at any temperature in the almost 4+ valence state, relying on various crystallographic and magnetic properties:

\(^1\) its a lattice parameter compared to

\(^2\) its a lattice parameter compared to

Figure 1: Thermal variations of the susceptibilities of YNi\textsubscript{5} and CeNi\textsubscript{5}.
that of the other RM₅ compounds (R = rare earth, M = Co, Ni, Cu) and the measurement of the LIII absorption edge of X-rays are characteristic of Ce⁴⁺, and (ii) the thermal expansion of CeNi₅ is quite analogous to that of the other RNi₅ compounds. Finally the susceptibility measured on a single crystal is practically isotropic at any temperature (figure 1) and cannot then be attributed to a 4f electron in an uniaxial surrounding. The maximum of the susceptibility around 100 K arises then from thermal smearing of the d electron density of state at the Fermi level, enhanced by the paramagnons. Such a behaviour can occur when the density of state at the Fermi level has a positive curvature(3) and is consistent with that observed in the Y-Ni compounds(4).

In order to evidence the origin of the susceptibility in CeNi₅, a study of the field induced magnetic density map by means of polarized neutron diffraction has been undertaken at various temperatures, especially at 100 K, temperature of the maximum of the susceptibility, and at 30 K, where the susceptibility is minimum.

**Experimental and results**

The single crystal was prepared by the Czochralski method using a water cooled copper crucible and an induction furnace and spark cut into a parallelepiped 5 x 5 x 0.5 mm³ with its short dimension along the neutron beam.

Measurements were performed on the D3 polarized neutron diffractometer of the I.L.L. A field of 46.2 kOe was applied parallel to the $c$-axis of the crystal and reflections (hk0) were measured out to $\sin \theta / \lambda = 0.75$ Å. The polarized beam technique yields essentially the polarization ratio $R = [(1+\gamma)/(1-\gamma)]^2$ with $\gamma = F_M/F_N$, $F_M$ and $F_N$ being the magnetic and nuclear structure factors respectively. More elaborate relations(5) are used to take into account corrections due to instrument imperfections and extinction effects. Moreover, a measurement using unpolarized neutrons was performed at 100 K on the 4 circle diffractometer D9, at various wave lengths in order to precisely determine the nuclear structure factors $F_N$ and the extinction parameters. The structure refinement has led to introduce a slight percentage of atomic random substitutions : 0.3 % of Ce atoms are replaced by Ni dumbells(6). The extinction parameters(7) are found to be : $t = 6.7 \pm 0.3$ μ and $g = 568 \pm 29$ ($\eta = 1.7 \pm 0.1$°).

The deduced magnetic structure factors $F_M$(hk0) for a section in reciprocal space lead by Fourier inversion to the projection of the induced magnetic density on the (001) plane. The value of the bulk magnetization is introduced as a constant $F_M$(000) term in the series. The diamagnetic susceptibility being of the order of $4 \times 10^{-4}$ μB/atom, it does not contribute to the results less than their standard deviation. The projections at 30 K and 100 K are shown on figure 2 as well as a scheme of the atomic projection. These projections evidence positive densities localized on the atomic sites : small values on the Ce atomic sites and larger values on the 2Ni sites. All the values are higher at 100 K than at 30 K. Following Brown and Wilkinson(8) we have obtained by a double Fourier transform the experimental "cylindrical form factors" for the 3 different atomic sites. These are compared on figure 3 to the Ni form

**Figure 2**: Projections of the magnetic densities in CeNi₅ at 30 K and 100 K, averaged on a square of 0.4 Å of side (contours are in $10^{-3}$ μB/Å²).
factor characteristic of 3d electrons, determined on Ni metal\(^9\)). Whereas the cylindrical form factors observed on the 2 Ni sites at 30 K are rather close to the Ni metal form factor, those observed at 100 K show a quite different decrease, corresponding to a much more localized density than in Ni metal. However, the same type of 3d electrons should mainly contribute to these densities and the observed localization must then result from the superposition of a contribution of 3d-type and of a strong antiparallel diffuse polarization which is non uniform. The value of the 3d moment is deduced by assuming that the observed form factor \(\text{f}_{\text{obs}}\) (figure 4) is then the superposition to the 3d Ni metal form factor \(\text{f}_{3d}\), of a negative contribution \(\text{f}_{\text{pol}}\) becoming null at \(\sin\theta/\lambda = 0.4 \text{ Å}^{-1}\).

The cylindrical form factor observed on the Ce sites is very unprecise and could then be fitted with a 4f-type form factor. Nevertheless it shows a decrease similar to that on the Ni sites and especially it becomes equal to zero for \(\sin\theta/\lambda = 0.9 \text{ Å}^{-1}\) while the form factor characteristic of Ce remains positive up to higher values of \(\sin\theta/\lambda\). It can then also be attributed to 3d electrons associated with a negative diffuse polarization. The values of all the moments induced by a 46.2 kOe applied field at 30 K and 100 K on the 3 atomic sites are reported in table I. The total localized magnetization obtained from this neutron study is compared to the bulk value given by the magnetization measurements. Their difference confirms at 100 K a large diffuse polarization, antiparallel to the 3d magnetism.
Table I: 46.2 kOe field induced magnetization in CeNi₅ (in 10⁻³ μₜₜ)

<table>
<thead>
<tr>
<th>T (K)</th>
<th>μ/Ni₂c</th>
<th>μ/Ni₃g</th>
<th>μ/Ce</th>
<th>μ/CeNi₅ localized</th>
<th>μ/CeNi₅ bulk</th>
<th>μ/CeNi₅ diffuse</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>4.8 (5)</td>
<td>4.8 (5)</td>
<td>2.3 (8)</td>
<td>26.3 (1.4)</td>
<td>26.3 (5)</td>
<td>0.0 (1.9)</td>
</tr>
<tr>
<td>100</td>
<td>7.0 (7)</td>
<td>8.2 (8)</td>
<td>2.9 (1.3)</td>
<td>41.5 (2.1)</td>
<td>28.3 (5)</td>
<td>-13.2 (2.6)</td>
</tr>
</tbody>
</table>

Discussion
In order to determine the origin of the maximum at 100 K of the bulk susceptibility we have compared on Table II the various contributions to this susceptibility at 30 and 100 K. One notices that the increase of the bulk susceptibility cannot be attributed to the increase of the susceptibility on the Ce sites, that is to a change of valence of the Ce atoms, but it is correlated to a much larger increase of the 3d character susceptibility measured on the Ni sites which is almost cancelled by the onset of a negative susceptibility characteristic of the diffuse polarization of conduction electrons with a s - 5d character.

Table II: Various contributions to the CeNi₅ susceptibility (in 10⁻⁶ μₜₜ/Ωe.mole).

<table>
<thead>
<tr>
<th>T (K)</th>
<th>Xbulk</th>
<th>XCe</th>
<th>X5 Ni</th>
<th>Xdiffuse</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>0.57 (1)</td>
<td>0.05 (2)</td>
<td>0.52 (2)</td>
<td>0.00 (4)</td>
</tr>
<tr>
<td>100</td>
<td>0.61 (1)</td>
<td>0.06 (3)</td>
<td>0.84 (4)</td>
<td>-0.29 (6)</td>
</tr>
</tbody>
</table>

In fact CeNi₅ is, like LaNi₅ or YNi₅, an enhanced Pauli paramagnet close to the onset of 3d magnetism. It can be compared to the compounds in the Y-Ni system with an Y concentration between YNi₅ and YNi₂ for which a resurgence of ferromagnetism is observed(10). Indeed, if we consider that Ce is 4+ in CeNi₅ whereas Y is 3+ in YNi₅, the alloy in the Y-Ni system with the same number of s - d conduction electrons would have the composition YNi₁₃₋₇₅ that is close to the compound Y₂Ni₇. This resurgence can be explained by an increase of the 3d - 4d hybridization as the Y concentration increases, involving an increase of the d density of states at the Fermi level(10). As well the 3d - 5d hybridization in CeNi₅ is larger than in YNi₅ leading to a larger value of the susceptibility in CeNi₅. Furthermore, as it can be seen on the scheme of the d density of states of the two compounds deduced from the calculations of Cyrot and Lavagna(11) (figure 5), the Fermi level in CeNi₅ (but not in YNi₅) lies in a zone of the density of states with a positive curvature. The maximum of the susceptibility arises then from the thermal smearing of the d electron density of states at the Fermi level, enhanced by the spin fluctuations.

The comparison of the local susceptibilities on the Ni atoms in YNi₅ or CeNi₅ confirms this interpretation. As a matter of fact, in YNi₅, it has been deduced from this comparison that the density of states at the Fermi level is lower for the 2c site than for the 3g site(12). In CeNi₅, an identical comparison shows that, on the contrary, the density of states at the Fermi level is higher for the 2c site than for the 3g site. This result is probably due to the different environments in Ce atoms for the 2 Ni sites, the Ni₂c being surrounded by 3 Ce atoms at rather short distances, thus leading to a stronger hybridization for the 3d electrons of that site.
The magnetization localized on the origin (la site) presents a form factor which, because of the low accuracy, can be attributed as well to a 4f-type as to a 3d-type moment. Because the Ce has been previously found to be almost in a 4+ valence state in CeNi$_5$ (2), we do not expect to find any significant 4f moment on the Ce atoms. Besides, this measured susceptibility on the la site could originate from the Ni dumbells substituted to 0.3% Ce atoms: it would correspond to a local susceptibility about 100 times larger than the CeNi$_5$ susceptibility. This is not unlikely if we consider that the local crystallographic structure in the substitution zones is that found in the Y$_2$Ni$_{17}$ compound which is ferromagnetic.

Figure 5: Scheme of the d density of states curves in YNi$_5$ (---) and CeNi$_5$ (----).

Acknowledgements

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References