NMR and NQR Studies of ^{61}Ni in Heavy Fermion Compounds Ce_7Ni_3

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(January 14, 2000)

The heavy fermion compound Ce_7Ni_3 is an antiferromagnet with T_N∼1.7 K. According to the high pressure experiment, this compound has undergone a transition to a non-Fermi liquid state at ∼0.32 GPa and has recovered a Fermi liquid state at ∼0.62 GPa again. Before the high pressure NMR study through two transitions, we have performed NMR experiments of ^{61}Ni, ^{59}Co and ^{63}Cu in order to clarify the electronic states at ambient pressure. Two kinds of partially overlapping Ni NMR spectra were observed in Ce_7Ni_3 containing an enriched ^{61}Ni. This result may be ascribed to two intrinsic local-fields presumably due to the lattice distortion etc. All the relaxation rates studied here are proportional to temperature above 1.4 K in the paramagnetic state, which indicates that the systems are in the Fermi liquid state at ambient pressure. The increase of $(1/T_1T)$ with increasing Co concentration, C_{Co}, tells us that the partial density of states on Ni-*3d* states at Fermi level, $N(E_F)_{Ni}$, increase with C_{Co}. On the contrary, C_{Cu} independent $(1/T_1T)$ values indicate $N(E_F)_{Ni}$ keep almost constant with Cu doping.

I. INTRODUCTION

A series of Ce- and U-based heavy fermion compounds possess various types of ground states. Among them, superconductivity at ambient pressure, paramagnetic phase with magnetic correlations and pressure induced superconductivity near the boundary between the paramagnetic and the magnetically ordered regimes, which are often accompanied by non-Fermi liquid (NFL) behaviors deviating from a conventional Fermi liquid (FL) concept, are especially attracting a great deal of attention in the area of strongly correlated electron systems. A parameter controlling physical properties is believed to be a strength in the hybridization between conduction electrons and *f*-electrons (the so called *c-f* hybridization), which is tuned by the substitution of constituent elements or the applied pressure. According to Doniach's phase diagram for the Kondo lattice, a competition between the RKKY and the Kondo interactions governs what types of ground states are realized.

Ce_7Ni_3 is a heavy fermion (γ=9 J/mol·K^2) [1] antiferromagnet with T_N∼1.7 K [2]. This compound crystallized in the hexagonal Th_7Fe_3-type structure with three inequivalent Ce sites, while there exists crystallographically just one Ni site. According to the recent neutron data [3], an SDW ordering appears around 1.9 K which originates from two sites of three Ce sites and a second transition around 0.7 K where only just one Ce site orders. With increasing pressure, T_N decreases and vanishes near p_c∼0.33 GPa [4]. NFL behavior appears at 0.4 GPa in the specific heat and the magnetic susceptibility measurements as $C_m/T \propto -\ln T$ and χ_{AC}∝(1-$\alpha T^{1/2}$), respectively. Above 0.62 GPa a conventional FL state recovers, as indicated by the T-independence in C_mT and the T^2-dependence in the magnetic resistivity [5]. Umeo *et al.* have reported that the observed crossover with pressure is described by the self-consistent renormalization (SCR) theory of spin fluctuations, which is applied to the heavy fermion systems near the antiferromagnetic instability by Moriya and Takimoto [6]. Among many heavy fermion compounds showing NFL behavior, a stoichiometric compound Ce_7Ni_3 is of particular interest, since the NMR study in Ce_7Ni_3 in general enables us to evaluate just an intrinsic line-width without any extra one accompanied by alloying. In addition, the T_N suppression to zero just on applying pressure as low as 0.4 GPa allows us to study the pressure-induced NFL behavior up to the FL regimes in an entire pressure range. In this paper we report the results of ^{61}Ni, ^{59}Co and ^{63}Cu NMR performed at ambient pressure on enriched ^{61}Ni, doped ^{59}Co and ^{63}Cu for probing Ni in order to clarify systematically the magnetic state and the mechanism involved.

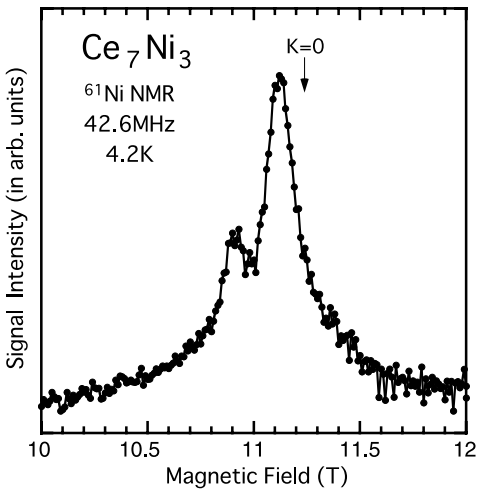

FIG. 1. NMR spectrum of ^{61}Ni in Ce_7Ni_3 obtained at 4.2 K. The arrow indicates K (Knight shift)=0.

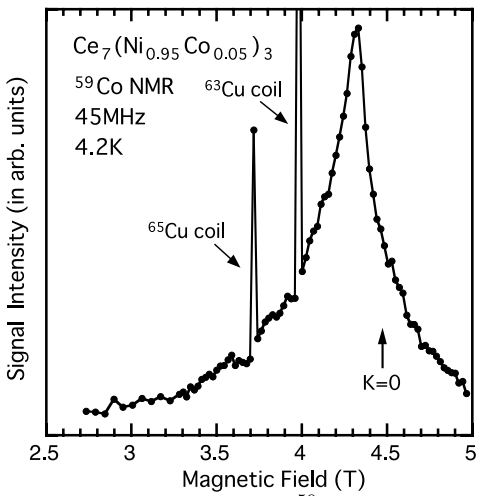

FIG. 2. NMR spectrum of ^{59}Co in $Ce_7(Ni_{0.95}Co_{0.05})_3$ obtained at 4.2 K. The arrow indicates K (Knight shift)=0.

II. EXPERIMENTAL

Polycrystalline ingots used in this study were prepared by argon arc melting and subsequent annealing. Starting materials for $Ce_7(Ni_{1-x}Co_x)_3$ and $Ce_7(Ni_{1-x}Cu_x)_3$ were Ce(99.9%), Ni(99.99%) and Co(99.99%). An enriched ^{61}Ni (^{61}Ni 99.44%, ^{58}Ni 0.13%, ^{60}Ni 0.19%, ^{62}Ni 0.05%, ^{64}Ni 0.19%, Oak Ridge National Lab.) powder was also employed for ^{61}Ni NMR and NQR measurements in Ce_7Ni_3. X-ray diffraction patterns showed all the samples formed the Th_7Fe_3 structure with a very small amount of impurity phase. The ingot was crushed into powder and sealed in a capsule with random alignment to magnetic field. The NMR experiment was carried out with a conventional phase-coherent spin echo spectrometer. The nuclear spin relaxation rates were measured by utilizing a saturation pulse method.

III. RESULTS AND DISCUSSION

Shown in Fig. 1 is the ^{61}Ni (I=3/2) NMR spectrum observed at 4.2 K in a field sweeping procedure. Since Ni atoms in Ce_7Ni_3 are crystallographically at sites with non-cubic symmetry, the electric quadrupole (eqQ) interaction with an electric field gradient, q of Ni (I=3/2) is fully expected. As shown in the figure, the spectrum composed of two kinds of Ni signals with about 2% of the difference in the resonance field was observed. Moreover, a weak Ni NMR signal taken at low field is hard to be assigned as a satellite signal in a typical eqQ pattern, because there is not the other signal observed at higher field. The two signals cannot be explained by two peaks split by the second-order quadrupole effect, because the separation between them is roughly proportional to the external field of 6 T $\sim$ 15 T. So this signal might be associated with Ni in some impurity phases or assigned to be Ni signal corresponding to one of two local-fields, which could be detected by NMR and exist just in non-doped Ce_7Ni_3. However, a signal observed at low field is too strong in comparison with the ratio of an impurity phase to a major phase found in the X-ray diffraction pattern. Thus, this weak signal might be not coming from Ni in some impurity phases but from Ni corresponding to one of two intrinsic local-fields, which is presumably due to the lattice distortion in Ce_7Ni_3.

Next, ^{59}Co NMR and NQR in $Ce_7(Ni_{0.95}Co_{0.05})_3$, $Ce_7(Ni_{0.9}Co_{0.1})_3$ and $Ce_7(Ni_{0.8}Co_{0.2})_3$ were performed in order to elucidate the electronic states at Ni in more detail. Fig. 2 shows the NMR spectrum of Co (I=7/2) in $Ce_7(Ni_{0.95}Co_{0.05})_3$. The ^{59}Co spectrum centered around 4.35 T cannot be simply explained by a well-separated quadrupole powder pattern with an almost equal separation. Wide line width of the Co NMR spectrum similar to Ni NMR indicates there exist wide distribution of q at Ni (Co) site, which is crystallographically just one site around three kinds of inequivalent Ce sites. Here, taking the electric quadrupole moment, Q for each nucleus into consideration, the observed line-width for each Ni (Co) NMR spectrum is well explained by three (seven) lines with almost equally separated satellites. Thus, the q-values for both Ni sites in Ce_7Ni_3 and Co sites in $Ce_7(Ni_{0.95}Co_{0.05})_3$ are considered to be almost same. Then, we have carried out the signal detection for Co in the frequency-range between 2 and 15 MHz under zero external field. Displayed in Fig. 3 is Co spectra observed around 5.63 MHz and 8.08 MHz in $Ce_7(Ni_{0.95}Co_{0.05})_3$ at 4.2 K. If these signals are assigned to the NQR signals corresponding to the transitions of $\pm1/2\rangle\Leftrightarrow\pm3/2\rangle$, $\pm3/2\rangle\Leftrightarrow\pm5/2\rangle$ ($\pm3/2\rangle\Leftrightarrow\pm5/2\rangle$, $\pm5/2\rangle\Leftrightarrow\pm7/2\rangle$), the third signal should be expected as 4.21 or 3.99 MHz (2.79 MHz) with the asymmetry parameter η=0.35 or 0.57 (0.57), respectively. However, the third signal for both cases was not observed. Considering the following three results; the increasing Co signal intensity with increasing Co concentration, no signal enhancement like ferromagnetic materials and no extra phase in X-ray diffraction pattern, two Co signals are considered to be Co NMR coming from (probably antiferro) magnetically ordered region due to the inhomogeneous distribution of Co around three inequivalent Ce sites. Next, the nuclear spin lattice relaxation rates, $(1/T_1)$'s of ^{61}Ni (I=3/2), ^{59}Co (I=7/2) and ^{63}Cu (I=3/2) were measured at the signal peak positions in the NMR spectra of Ce_7Ni_3, Co-doped and Cu-doped Ce_7Ni_3 systems, respectively. Fig. 4 shows the temperature dependence of $(1/T_1)$'s above 1.4 K. If the excitation between nuclear spin levels for ^{61}Ni and ^{63}Cu (I=3/2) could be achieved with a weak pulse as to saturate only $\pm1/2$ levels, the T_1 values were fitted to the following recovery equation [7],

$$\frac{M(\infty)-M(t)}{M(\infty)} = 0.1\exp(-\frac{t}{T_1}) + 0.9\exp(-\frac{6t}{T_1}),$$

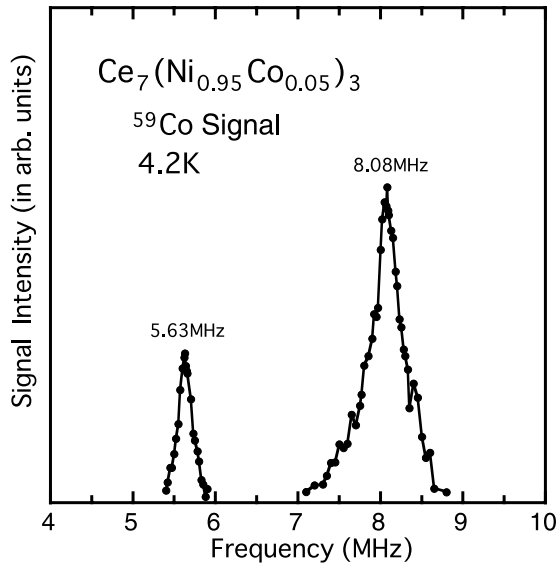

FIG. 3. NMR spectra of ^{59}Co in $Ce_7(Ni_{0.95}Co_{0.05})_3$ obtained at 4.2 K. (see text)

where $M(t)$ is the nuclear magnetization recovery at the variable delayed time t after the saturation of the central line. Quite similarly, the T_1 value of ^{59}Co (I=7/2) NMR signal was also obtained by monitoring $M(t)$. In this case the $M(t)$ is given by

$$\frac{M(\infty)-M(t)}{M(\infty)} = 0.012\exp(-\frac{t}{T_1}) + 0.068\exp(-\frac{6t}{T_1}) + 0.206\exp(-\frac{15t}{T_1}) + 0.714\exp(-\frac{28t}{T_1}).$$

Here, according to our susceptibility measurement, the Co- and Cu-doped systems are found to have the lower T_N's than that (1.7 K) in Ce_7Ni_3. As shown in Fig. 4, three kinds of relaxation rates, $(1/T_1)$'s, of ^{61}Ni, ^{59}Co and ^{63}Cu vary in proportion to temperature (Korringa rule), which indicates that both paramagnetic systems set in the Fermi liquid state above 1.4 K. As is well known, $(1/T_1)$ is proportional to the square of the density of states at Fermi level, $N(E_F)$, times the square of the hyperfine coupling constant, A_{hf}, at a respective site. Since the A_{hf} at Co site, A_{hfCo} deduced from the susceptibility vs. the Knight shift on Co keeps almost constant on increasing Co concentration, C_{Co}, the increase of $(1/T_1T)$ with increasing C_{Co} tells us that the partial density of states on Ni-*3d* states at Fermi level, $N(E_F)_{Ni}$, increase with C_{Co}. On the contrary, C_{Cu} independent $(1/T_1T)$ values indicate $N(E_F)_{Ni}$ keep almost constant with Cu doping, if A_{hfCu} stays constant.

In summary, two kinds of partially overlapping ^{61}Ni NMR spectra were observed in Ce_7Ni_3 containing an enriched ^{61}Ni. This result may be ascribed to two intrinsic local fields presumably due to the lattice distortion. Two ^{59}Co (I=7/2) signals observed at 5.63 MHz and 8.08 MHz in Co-doped Ce_7Ni_3 were are considered to be Co NMR coming from magnetically ordered region due to the inhomogeneous distribution of Co around three inequivalent Ce sites. All the relaxation rates of ^{61}Ni, ^{59}Co and ^{63}Cu are proportional to temperature above 1.4 K in the paramagnetic state, which indicates that all the systems are in the Fermi liquid state. Further NMR studies under high pressure are now in progress.

This work is partially supported by a Grant-in-Aid from the Ministry of Education, Science, Sports and Culture of Japan.

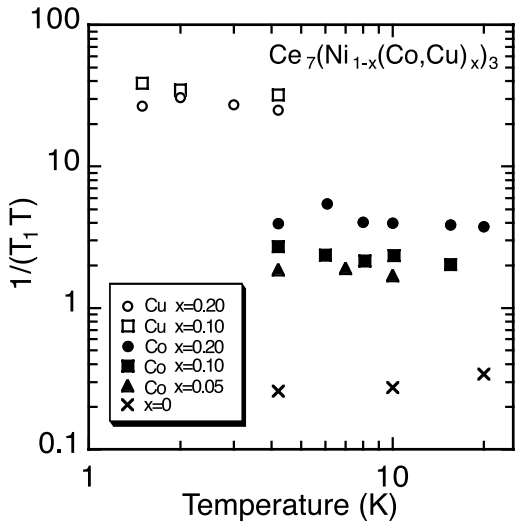

FIG. 4. Temperature dependence of nuclear spin relaxation rates times temperature of ^{61}Ni, ^{59}Co and ^{63}Cu in Ce_7Ni_3, Co- and Cu-doped systems. They are shown as crosses, triangles, squares and circles for 0%, 5%, 10% and 20% of impurity concentrations, respectively. The closed and open symbols are the $(1/T_1)$'s of ^{59}Co and ^{63}Cu, respectively.

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