NMR spectral study under zero external field in pure and diluted CeRhIn$_5$ by La substitutions

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Abstract. CeRhIn$_5$ is an incommensurate antiferromagnet with $T_N = 3.8$ K. The NMR spectra for tetragonal In(1) sites in CeRhIn$_5$ have been investigated under zero applied field in order to distinguish between spin density wave or spiral order. The $^{115}$In(1)-NMR spectra around $2
\nu_Q$ under zero field below $T_N$ provide a good indication of spiral order. The La substitutions of 1 % and 2 % indicate a decrease of the internal field on In(1) sites due to the reduction of hyperfine couplings by La substitutions.

1. Introduction

CeRhIn$_5$ belongs to the so-called 115 family which has a tetragonal HoCoGa$_5$ type structure. At ambient pressure, CeRhIn$_5$ is an antiferromagnet below $T_N = 3.8$ K [1]. Unconventional superconductivity emerges under applied pressure, reaching a maximum transition temperature $T_c = 2.1$ K near the critical pressure $P_c = 2.5$ GPa where the antiferromagnetic transition extrapolates to $T = 0$. Recent de Haas-van Alphen (dHvA) measurements reveal a divergence of the effective mass close to $P_c$, consistent with proximity to an antiferromagnetic (AFM) quantum critical point (QCP) [2]. The dHvA frequencies of principal orbits increase sharply, as if signaling a transition from small-to-large Fermi volume, which is interpreted as a localized/itinerant crossover of the 4$f$ electrons at the QCP. At ambient pressure, the incommensurate AFM order of Ce moments with propagation of $Q = (1/2, 1/2, 0, 0.297)$ has been reported by neutron diffraction experiments [3]. Zero-field $^{115}$In NMR measurements on a powder sample of ground single crystals [4] have proposed that such an incommensurate AFM order originates from a spiral arrangement of Ce moments, not from spin-density wave (SDW) modulation of Ce moments. There are two crystallographically inequivalent In sites denoted In(1) (1$c$ site) and In(2) (4$i$ site). The In(1) sites have axial symmetry in the Ce-In planes, but the In(2) sites have two Ce and two Rh neighbors in the a planes and, thus, lower symmetry. As discussed below, key data necessary to conclude spiral order is $^{115}$In(1)-NMR spectra under zero field; although, In(2)-NMR has deduced clear evidence about the incommensurability. As for the previous In(1) spectra in the AFM state [4, 5], data points were scarce and insufficient to distinguish unambiguously between SDW or spiral cases. In this proceedings paper, we look more carefully into the zero-field $^{115}$In(1)-NMR spectra and report the change of internal fields on In(1) sites by dilute La substitutions of 1 % and 2 %.
In(1)-NQR spectra at 10 K and NMR spectra at 1.6 K for pure CeRhIn$_5$ under zero applied field. Panels (a), (b) and (c) show spectra taken around 2$\nu_Q$, 3$\nu_Q$ and 4$\nu_Q$ lines of $^{115}$In(1) sites, respectively. The lower shaded spectra are simulated in the cases of spiral and spin-density-wave (SDW) ordering of Ce moments.

2. Experimental

Single crystals of Ce$_{1-x}$La$_x$RhIn$_5$ ($x = 0.0, 0.01, 0.02$) were grown by a self-flux method. NQR and NMR measurements in the temperature range 1.5-100 K were performed using a conventional phase-coherent pulsed NMR spectrometer. Frequency-swept spectra under zero field were measured in the frequency range of 10-30 MHz. One piece of single crystal was mounted into an rf-coil in order to avoid decompositions and/or surface strains by crushing the crystals. This is important because powdering or crushing CeRhIn$_5$ influences physical properties, especially, the volume fraction of incommensurate/commensurate antiferromagnetism and parasitic superconductivity [6, 7].

Using conventional notation, the quadrupole frequency parameter is defined as $\nu_Q = \frac{3e^2qQ}{2I(2I-1)}$, where $eQ$ is the nuclear quadrupolar moment, $I$ is the nuclear spin quantum number, and $eQ \equiv V_{ZZ}$ is the principal component of the electric field gradient (EFG) tensor. Here, $V_{ii}$ denotes EFG tensor components in the principal coordinate system, such that $|V_{XX}| \leq |V_{YY}| \leq |V_{ZZ}|$ for each ionic site.

3. Results and discussions

Figure 1 shows the In(1) NQR spectra at 10 K (above $T_N$) and NMR spectra at 1.6 K (below $T_N$) for CeRhIn$_5$ under zero field. In the paramagnetic state, the NQR spectra show narrow line widths of $\sim$50 kHz at each of the transition lines: 2$\nu_Q$, 3$\nu_Q$, and 4$\nu_Q$. These sharp lines indicate negligible lattice disorder in this high quality crystal. The $\nu_Q$ is determined to be 6.778 MHz at 10 K for $^{115}$In(1) sites, which is consistent with previously reported values [4, 5]. Generally, in an AFM ordered state nuclei experience site-specific internal fields and NMR spectra with zero applied field can be observed that exhibit characteristic features of the ordered state. As already reported for CeRhIn$_5$ in its ordered state [4], zero-field NMR spectra for In(2) show a double-horn type pattern, like a powder-pattern, which is known to be characteristic of incommensurate order. The internal field on the In(2) sites can be expressed as $H_{int} = A|\mathbf{M}(n)|$, where $A$ is the transferred hyperfine coupling constant and $\mathbf{M}(n)$ is the Ce staggered moment in the $ac$ plane. Neutron diffraction has revealed that Ce moments lie in the $c$-plane and that the propagation vector is $\mathbf{Q} = (1/2, 1/2, \delta \equiv 0.297)$. In the case of SDW order, $|\mathbf{M}(n)| \propto \sqrt{T+\cos(4\pi n\delta)}$, that is, the magnitude of Ce moments modulates along the $c$ axis.
On the other hand, in the case of spiral order, $|M(n)| = M$ is constant, while $M(n)$ points spirally as $M(n) = M(\cos(2\pi n\delta), \sin(2\pi n\delta), 0)$. In the both cases of SDW and helical order, the internal field $H_{\text{int}}$ on In(2) sites is parallel to the $c$ axis and oscillates as $\alpha \cos(2\pi n\delta)$, that is, we can not distinguish whether it is SDW or spiral from In(2) spectra.

As for In(1) sites, $H_{\text{int}}$ on In(1) sites is independent of $n$ in the case of spiral order, but $H_{\text{int}}$ oscillates as $\alpha \cos(2\pi n\delta)$ in the case of SDW order. The direction of $H_{\text{int}}$ is perpendicular to the $c$ axis in the both cases. The simulated spectra for In(1) sites are shown in Fig. 1. These spectra were calculated by numerical diagonalization of the Hamiltonian matrix, including Zeeman ($\gamma_N h \mathbf{I} \cdot \mathbf{H}_{\text{int}}$) and quadrupolar terms. These simulated spectra also are convoluted by a Gaussian function with a natural width of 50 kHz. Values of $\nu_Q = 6.778$ MHz and $H_{\text{int}} = 1.59$ kOe are used for the simulations. As shown in Fig. 1(b) and (c), the simulated spectra are similar for both cases around $3\nu_Q$ and $4\nu_Q$ lines; whereas, the spectra around $2\nu_Q$ become distinct in appearance for SDW and spiral ordering. It is noteworthy that finite spectral weight should be observed around 13 MHz in the SDW case and that the spectra should have finite weight even below $\sim 12$ MHz. As shown in Fig. 1(a), however, spectral weight in the measured spectrum around 13 MHz is zero within the experimental accuracy, and there is no observed intensity below $\sim 11.5$ MHz (down to 10 MHz in this experiment). Therefore, we can conclude that spiral order in CeRhIn$_5$ is highly plausible as proposed in Ref. [4]. A definite amplitude of Ce moments in such a spiral order also indicates the localized nature of 4$f$ electrons in CeRhIn$_5$.

Next, we have investigated the change of $H_{\text{int}}$ by La substitutions of 1 % and 2 %. Temperature variations of the $4\nu_Q$ line for CeRhIn$_5$ and lightly La-substituted CeRhIn$_5$ are shown in Fig. 2(a). Using similar calculations as discussed above, $4\nu_Q$ NMR in the ordered state also can be interpreted as $H_{\text{int}}$ on In(1) sites. Estimates of $H_{\text{int}}$ on In(1) sites are shown in Fig. 2(b). $H_{\text{int}}$ decreases from 1.59 kOe in pure CeRhIn$_5$, to 1.48 kOe in 1 %-La, and 1.26 kOe in 2 %-La substituted CeRhIn$_5$, which corresponds to a reduction of $H_{\text{int}}$ by 20 % with only 2 % La substitution. Although $H_{\text{int}}$ is reduced, neutron diffraction measurements have revealed that La substitution of 1 % does not affect the size of the ordered Ce moment nor the incommensurate propagation $\delta$ [8]. So, the change of $H_{\text{int}}$ probably originates mainly from a change of transferred hyperfine coupling constant $A$, not from the change of Ce moment $M$. Indeed, we also have detected a change in the diagonal term of the hyperfine coupling
tensor in the paramagnetic state. The $a$ component $A_a$ for CeRhIn$_5$, Ce$_{0.99}$La$_{0.01}$RhIn$_5$, and Ce$_{0.98}$La$_{0.02}$RhIn$_5$ is estimated to be $18.3$, $15.8$, and $10.4$ kOe/$\mu_B$, respectively. Here, $A_a$ is defined from the slope in a plot of Knight shift versus static susceptibility with temperature as an implicit parameter. Because the hyperfine coupling is often changed between ordered and paramagnetic states, it is difficult to estimate quantitatively the corresponding moment size on Ce ions in the ordered state. Moreover, the existence of off-diagonal hyperfine coupling in the ordered state of CeRhIn$_5$, discussed in Ref. [9], would impose difficulty in estimating $M$ from NMR experiments. We can say, however, that the transferred coupling on In(1) sites is sensitive to dilute La substitutions. The reduction of $T_N$ by La substitutions [10] may come from the reduction of exchange couplings, which has been suggested microscopically from nuclear spin-lattice relaxation rates $1/T_1$ (not shown). Detailed results of $1/T_1$ will be presented elsewhere. In this regard, we also note that the reported pressure-induced change of $H_{\text{int}}$ [5] seems to be due to the change of $A$, because neutron diffraction could not observe a corresponding reduction of $M$ by pressure [11].

4. Conclusion
We have investigated the antiferromagnetically ordered state of CeRhIn$_5$ by NMR/NQR techniques. Specifically, we have focused on In(1) NMR spectra under zero applied field to conclude spiral order. As a result, AFM spiral order is highly plausible as suggested previously. A uniform moment on Ce ions is consistent with a localized nature of $4f$ electrons in CeRhIn$_5$. Lanthanum substitutions of 1 % and 2 % reduce the internal field on In(1) sites, coming from the change in transferred hyperfine coupling via $p$-$f$ mixing.

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