Physica B 405 (2010) 4691–4695

Contents lists available at ScienceDirect

Physica B

journal homepage: www.elsevier.com/locate/physb

^{27}Al and ^{63}Cu NMR studies on intermetallic Kondo compound $CeCu_3Al_2$

B. Bandyopadhyay *, M. Majumder, A. Ghoshray, K. Ghoshray

Saha Institute of Nuclear Physics, 1/AF Bidhannagar, Kolkata 700 064, India

ARTICLE INFO

Article history:
Received 19 July 2010
Accepted 27 August 2010

Keywords:
Intermetallic compound
Kondo system
Knight shift
Spin-lattice relaxation

ABSTRACT

Detailed ^{27}Al and ^{63}Cu nuclear magnetic resonance (NMR) experiments have been performed in between 4.5 and 295 K on a polycrystalline sample of $CeCu_3Al_2$ which has a Kondo temperature ~ 11 K. The NMR spectral features and Knight shift measurements show that in this compound, Cu occupy both c and g lattice sites, while Al occupy only the g sites. From the temperature dependence of Knight shift (K), the hyperfine fields for ^{63}Cu and ^{27}Al at the g sites have been estimated as 2.02(5) and 1.67(5) kOe/μ_B, respectively, and that for ^{63}Cu at c sites as $-3.83(5)$ kOe/μ_B. Nuclear spin-lattice relaxation time (T_1) measurements indicate that though the relaxation process is governed by fluctuations of magnetic interaction, nuclear quadrupolar interaction also has a significant contribution, especially towards relaxation of ^{63}Cu in both c and g sites. For ^{27}Al, K and T_1 have yielded the effective 4f-spin correlation rate $1/\tau_{4f}$. The behavior of its temperature dependence indicates that at low temperatures in $CeCu_3Al_2$, the valence state of cerium might not be stable.

1. Introduction

Rare earth-based intermetallic compounds with localized 4f electron moments are often characterized by a competition between RKKY interaction which facilitates long-range magnetic ordering, and Kondo interaction that screens the localized moments. An easy way of changing or tuning the physical properties of such compounds is the substitution of one or some of the constituent elements. AB_5 (A=rare earths, B=Co, Ni, and Cu) [1] compounds form hexagonal $CaCu_5$ structure with A in a: 0,0,0; and B in 2*c*: $\pm$ (1/3,2/3,0), and 3*g*: 1/2,0,1/2; 0,1/2,1/2; 1/2,1/2,1/2. Many of these compounds show interesting changes in their physical properties when the B element is partially replaced by Al. For example, $CeCu_5$ is a magnetically ordered Kondo compound with Kondo temperature, T_K, of ~ 5.5 K and antiferromagnetic transition at ~ 4 K [2]. Al substituted compounds $CeCu_4Al$ and $CeCu_3Al_2$, both show Kondo behavior with $T_K > 5.5$ and ~ 11 K, respectively. However, while in $CeCu_4Al$ the possibility at 0.5 K of a magnetic phase transition is not excluded, there is no indication of such a transition in $CeCu_3Al_2$ down to 30 mK [2]. $SmCu_5$ is antiferromagnetic below 9 K [3], whereas $SmCu_3Al_2$ shows ferromagnetic transition at 12 K [4]. $GdCu_5$ is likely to have a complex magnetic structure [5] and shows antiferromagnetic transition at 12.5 K, but in $GdCu_3Al_2$ ferromagnetism is obtained below 20 K [4]. In all these examples, substitution of Cu by Al preserves the hexagonal structure, with Al predominantly in g sites [4].

Though various studies were performed on parent AB_5 compounds, there have been very little studies on Al substituted materials, and so far there is no report of microscopic investigations into the effect of Cu/Al substitution. Here we present detailed ^{27}Al and ^{63}Cu nuclear magnetic resonance (NMR) experiments on $CeCu_3Al_2$ in between 4.5 and 295 K. This compound shows Curie–Weiss (CW) behavior in magnetic susceptibility at temperatures above 50 K, resistivity maximum at 2.8 K, thermopower maximum below 50 K and Kondo temperature variously estimated as 10–11 K [2,4]. Moreover, an electronic contribution of specific heat (c_p/T) showed a broad maximum with the peak value of 490 mJ/mol K^2 at 1.9 K, which can be interpreted as the coherence temperature [6] that is characteristic of non-magnetic localized moment systems. Isostructural compound $LaCu_3Al_2$ [4] was used as reference for the analysis of NMR data.

2. Sample preparation and characterization

The compounds were prepared from high-purity elements by arc-melting in purified argon atmosphere, and subsequently annealed at 873 K for 7 days. X-ray powder diffraction measurements show the formation of single phase compounds belonging to $P\,6/mmm$ space group with $a = 0.5260$ nm and $c = 0.4177$ nm for the Ce compound, and $a = 0.5295$ nm and $c = 0.4186$ nm for the La compound, agreeing well with the published data [4]. Magnetic susceptibility measurements on $CeCu_3Al_2$ at temperatures $2 \leq T \leq 300$ K resemble the published results [2,7,4], i.e., CW behavior at temperatures above 50 K with paramagnetic Curie

---

* Corresponding author. Fax: +91 33 2337 4637.
E-mail address: bilwadal.bandyopadhyay@saha.ac.in (B. Bandyopadhyay).

0921-4526/\$ - see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.physb.2010.08.065

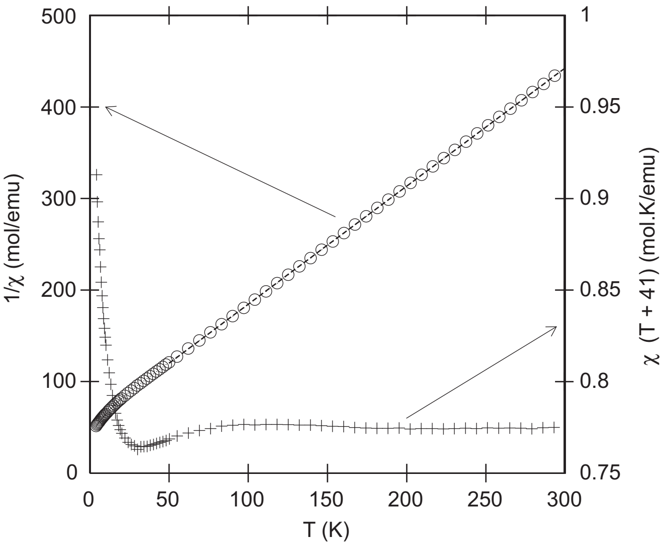

Fig. 1. Temperature (T) dependence of inverse of magnetic susceptibility ($1/\chi$) ($\odot$, left y-axis), and $\chi(T+\theta_p)$ with $\theta_p=41$ K (+, right y-axis) in $CeCu_3Al_2$. In $1/\chi$ vs T plot, the Curie–Weiss behavior above 50 K is shown by the broken line.

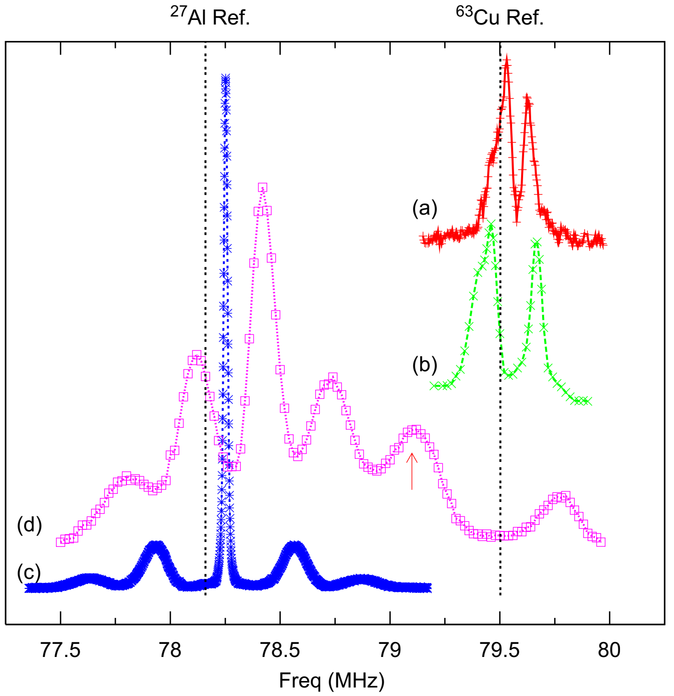

Fig. 2. NMR spectra in $CeCu_3Al_2$. (a) and (b) are ^{63}Cu spectra in 295 and 160 K, respectively. (c) is ^{27}Al spectrum at 295 K, and (d) is composite ^{27}Al and ^{63}Cu spectrum at 40 K in which the arrow marks the position of overlapping ^{63}Cu(c) line and $+3/2\leftrightarrow+5/2$ line of ^{27}Al. Broken lines joining discreet points in the spectra are guide to the eye. Vertical broken lines mark the positions of ^{27}Al and ^{63}Cu references.

temperature (θ_p) of 41 K and effective moment $2.49\mu_B$/Ce ion (μ_B is the Bohr magneton). Fig. 1 shows the experimental $1/\chi$ vs T plot of $CeCu_3Al_2$ and the fitting with the CW equation with the above-mentioned parameters. Also shown in this figure is the deviation from CW behavior through the $\chi(T+\theta_p)$ vs T plot. As temperature is decreased below 50 K, the increase in χ first becomes slower than that predicted by CW law, goes through a minimum near 30 K, and then becomes much faster. Such a behavior of magnetic susceptibility suggests the presence of crystal fields, though crystal fields alone cannot explain the result [8]. On the other hand, it appears from the published literature that this kind of susceptibility behavior might have been exhibited earlier in $YbAlCu_4$ [9] and $La_{0.4}Yb_{0.6}Cu_3Al_2$ [10], compounds showing signs of Yb valence instability.

3. Nuclear magnetic resonance (NMR) measurements

3.1. NMR spectra and Knight shift

^{27}Al and ^{63}Cu spectra in $CeCu_3Al_2$, narrow at higher temperatures and quite broad at lower temperatures, as shown in Fig. 2, were obtained using appropriate methods [11]. At 295 K, the spectrum of ^{27}Al (spin $I=5/2$) in $CeCu_3Al_2$ (Fig. 2c) shows a very strong central transition at a resonance frequency higher than that of ^{27}Al reference, and accompanied with comparatively weak but well-separated pairs of satellite transitions on both sides. A theoretical fit of the spectrum involving anisotropic Knight shift and nuclear quadrupolar interaction yields an isotropic shift of 0.118(1)%, quadrupolar coupling constant (QCC) of 0.7 MHz and asymmetry (η) of 0.1. With decrease in temperature, the same spectrum is gradually broadened and its shift increases. Spectral features clearly show that Al in $CeCu_3Al_2$ occupy only one type of sites, and it should be the g sites, as indicated by crystallographic studies [4]. $LaCu_3Al_2$ yields a similar ^{27}Al resonance line with five transitions and a temperature independent shift of 0.065% in between 80 and 295 K.

On the other hand, the spectrum at 295 K of ^{63}Cu ($I=3/2$) in $CeCu_3Al_2$ consists of two resonance lines, both shifted to high frequency side of the reference position. Unlike ^{27}Al, both the ^{63}Cu resonance lines are very much broadened due to anisotropic Knight shift and nuclear quadrupolar interaction, and the satellite transitions are not discernible. The shifts are determined at the position of the peak for both the resonance lines. With decrease in temperature, the shift of one of the lines increases, and that of the other decreases, as shown in Fig. 2a and b. Comparing with the behavior of ^{27}Al resonance, we assign the former ^{63}Cu resonance line as ^{63}Cu(g), i.e., arising from Cu in g sites, and the later as ^{63}Cu(c). At around 40 K, ^{63}Cu(c) resonance line merged with the $+3/2\leftrightarrow+5/2$ transition line of ^{27}Al (Fig. 2d), and no measurements on ^{63}Cu(c) line were possible below 40 K. $LaCu_3Al_2$ yields a single ^{63}Cu resonance line in between 80 and 295 K. The width of this line, when compared with that of ^{63}Cu resonance lines of $CeCu_3Al_2$, suggests that it might actually be a superposition of two lines originating from two different Al sites. The difference in their positions is comparable with the width of the lines, so that they appear as a single line with a temperature independent shift of 0.12%.

In systems with localized magnetic moments, the total shift (K) is expressed as a sum of a temperature independent part (K_0) and a temperature dependent part that is linear with molar magnetic susceptibility (χ) due to localized moments, as given by,

$$K=K_0+(H_{hf}/N\mu_B)\chi. \tag{1}$$

In above equation, H_{hf} is the hyperfine field at the nucleus. Fig. 3 shows the fractional shift of the central transition of ^{27}Al resonance line and the two ^{63}Cu resonance lines as a function of temperature, and also as a function of χ with temperature as an implicit parameter. In case of ^{27}Al, K vs χ plot is linear in between 35 and 295 K, and Eq. (1) yields $K_0=0.050(5)\%$ and $H_{hf}=1.67(5)\,\mathrm{kOe}/\mu_B$. A similar plot yield $K_0=0.075(5)\%$ and $H_{hf}=2.02(5)\,\mathrm{kOe}/\mu_B$ for ^{63}Cu(g), for which K vs χ seems to be linear almost down to 10 K. In case of ^{63}Cu(c) in between 50 and