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^{59}Co NMR AND NUCLEAR MAGNETIC RELAXATION STUDY OF THE MAGNETIC SUPERCONDUCTOR Y_9Co_7†

by

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ABSTRACT

The magnetic superconductor Y_9Co_7 presents in its structure magnetic and non-magnetic Co atoms. A search was made of the ^{59}Co NMR lines attributed in the literature to magnetic Co atoms, with negative results. For the strong ^{59}Co NMR line arising from nuclei of non-magnetic Co atoms the relaxation times T_1 and T_2 versus temperature were measured directly at 6.5 MHz and 9.0 MHz. A linear dependence on temperature was observed for $1/T_1$ which can be attributed to interactions with conduction electrons. $1/T_2$ is not linear with temperature, an effect that is related to the temperature dependence of the magnetization.

Key-words: Y_oCo_7; NMR; Nuclear magnetic relaxation.

1. INTRODUCTION

The intermetallic compound Y_9Co_7 (described in the first studies as Y_4Co_3) contrasts with other magnetic superconductors since its magnetism arises from d band electrons. Its superconducting transition falls below the Curie temperature (Ts = 2K, Tc = 4.5K) (1). This system has been investigated with several techniques (for a review see (2)) including NMR (3, 4, 5, 6). These studies have revealed that in this compound there are cobalt atoms that carry magnetic moments of the order of $0.1\mu_B$. It is now established that the majority of Co atoms which occupy 6h type positions in the structure are nonmagnetic. There is also suggestion that the cobalt atoms on the 2b and 2d type positions carry magnetic moments: there is no agreement on the NMR line frequencies corresponding to these magnetic atoms (3,5). Figiel and others (3) report in their spectra obtained at 9.12 MHz, a line at 0.66 T, while Wada and co-authors (6) have found one at 18 MHz (Bext =0). The ^{59}Co nuclear relaxation rate $1/T_1$ of the paramagnetic Co line follows a Korringa relation for $T > T_c$, and shows a non-linear behaviour below 30K, according to ref. (6). The measurement of T_1 (ref. (6)) was made indirectly, from the intensity of the two-pulse spin echoes.

In the present work we had two goals: to re-examine the NMR line corresponding to magnetic Co atoms, in view of conflicting reports, and afford a direct measurement of T_1 and T_2 of the paramagnetic line with temperature, to allow a discussion of the non-linear behaviour described in (6).

2. EXPERIMENTAL DETAILS

The measurements were made using a Bruker SXP spin-echo spectrometer, in the temperature range 1.5K-4.2K, with and without external magnetic field. The data acquisition system was based on a box-car integrator and a microprocessor.

The sample of Y_9Co_7 used was prepared from the same ingot as used by Kolodziejczyk and Sulkowski (8). It was crushed to a grain size 0.1 - 0.3 mm: the larger size of the grains was necessary to avoid suppressing superconductivity. The grain size of the powdered sample used by Takigawa et al. (5) and Wada et al. (6) was much smaller, and this smears out the superconducting transition. The powder was sealed with silicone oil in plexiglass tubes. Silvered coils were used to improve the quality factor of the resonant circuit and to reduce the intensity of the Cu lines. The sensitivity of the coils was tested with proton resonance both for a sample of copper sulphate solution and in the sample holder and oil. The proton signal was easily visible at room temperature, and at helium temperatures it was comparable to the ^{59}Co echo. In spite of silvering the coils, Cu lines were still observed due to the relatively large penetration depths of the electromagnetic waves into the wire.

The nuclear relaxation time T_1 was measured using a sequence of three $\pi/2$ pulses recording the stimulated echo height versus separation between the second and third pulses. To determine T_2, two pulses were used, and the echo amplitude was measured as a function of pulse separation. In either case the repetition time was sufficiently long (up to 200 ms) to enable the system to return to thermodynamic equilibrium.

3. NMR SPECTRA

The NMR spectra obtained at 2.0 K and 4.2 K, (Fig. 1) taken at 10.15 MHz, exhibit a strong peak at 1.00 T, corresponding to a Knight shift of 0.95% (using $\gamma/2\pi$ = 10.054 MHz/T). Following earlier studies (3, 4, 5, 6) we associate this line to Co atoms in sites 6h and 2d; the main contribution at the peak comes from the 6h site. Only a small hump is visible between 0.7 and 0.8 T, in contrast to the line previously reported in this region (3, 4).

We have made a search for the very broad line (about 9 MHz wide) reported at 18 MHz (5) without external field. We have varied the temperature in the range 1.5-4.2K, length and separation between pulses (from 0.5 μs to 200 μs) and repetition rates (from 1 Hz to 1 kHz) and failed to detect this line. An external field in the range of zero to 1.2T was also applied without success in the detection of the line.

We have therefore not been able to observe any of the two lines reported in references (3, 4) and (5) and suspect that they probably arise from variations in sample preparation, or maybe, in the first case, from the presence of other nuclei in the sample holder and surface effects on the grains. Due to the very small size of the grains reported in (5), Co atoms near the mechanically distorted surface may have different magnetic properties, and contribute with relatively strong signals. We have in our search taken into account the fact that the line corresponding to magnetic Co atoms would change its position significantly with temperature. This follows from the temperature dependence of the magnetization (8) and from the linear relation between hyperfine field and magnetic moment (assuming only d electrons).

The expected intensity of the magnetic line would be approximately 1/3 or 1/5 of the paramagnetic line for an enhancement factor $\eta = 1$, or even larger if $\eta > 1$.

4. NUCLEAR RELAXATION TIMES

The ^{59}Co nuclear relaxation times T_1 and T_2 were measured at the maximum amplitude of the paramagnetic line at 9.0 MHz (corresponding to a field of 0.89 T) and at 6.5 MHz (field of 0.63 T). These maxima were determined with an uncertainty of 0.01 T. The corresponding Knight shifts are in agreement with the values given in (5) and (6). The changes in relaxation time within the maximum of the line were of the order of 10%.

The curves of $1/T_1$ and $1/T_2$ versus temperature are shown for 9.0 MHz and 6.5 MHz in Fig. 2. The experimental points for $1/T_1$ show a fairly good fit to a straight line: the angular coefficients are $45.5 \pm 2\ (sK)^{-1}$ (9.0 MHz) and $37.6 \pm 2\ (sK)^{-1}$ (6.5 MHz), respectively. The transversal relaxation rate $1/T_2$ depends non-linearly on temperature; the points for the two frequencies (or two values of applied magnetic field) are significantly displaced. The values at 6.5 MHz are some 20% higher than those observed at 9.0 MHz.

5. DISCUSSION

To comment on the temperature dependence of the relaxation rates, we recall the general expression relating $1/T_2$ and $1/T_1$ (9):

$$\frac{1}{T_2} = \frac{1}{2T_1} + \gamma_n^2 \int_{-\infty}^{\infty} \langle\{\delta H^z(t)\,\delta H^z(o)\}\rangle_s \, dt \qquad (1)$$

where the term under the integral is the correlation function for the fluctuation of the transverse component of the local field at the nucleus.

The linear dependence with T observed for $1/T_1$ at both frequencies suggests a predominance of conduction electron effects. However, to explain our $1/T_2$ results it is required that the second term of Eq. (1) varies non-linearly with T. The superconductivity cannot influence relaxation rates because it is suppressed by external magnetic field (7) in this case. Since the hyperfine fields at the Co nuclei under consideration are transferred from the neighbours, the fluctuations in the integral arise at least in part from the fluctuations of the atomic moments of the magnetic Co neighbours, what suggest correlation of $1/T_2$ temperature dependence with magnetic moment changes versus temperature.

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FIGURE CAPTIONS

Fig. 1. Y_9Co_7 NMR spectrum obtained at 4.2 K (f = 10.15 MHz). Two lines, due to ^{63}Cu and ^{65}Cu resonances, are also visible.

Fig. 2. Relaxation rates $1/T_1$ and $1/T_2$ versus temperature, measured at 6.5 MHz and 9.0 MHz.

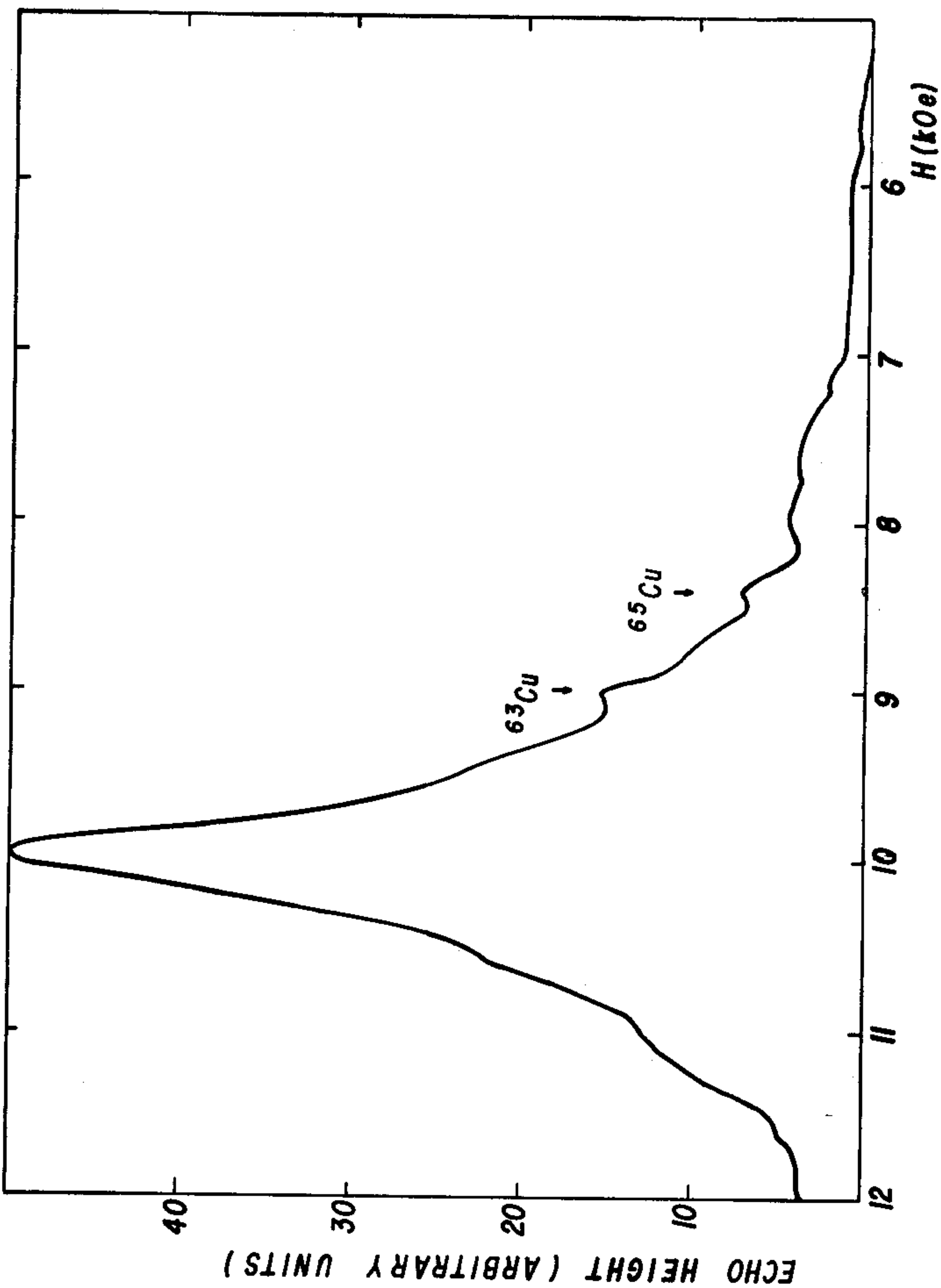
ECHO HEIGHT (ARBITRARY UNITS)
10
20
30
40
H (kOe)
6
7
8
9
10
11
12
^{63}Cu
^{65}Cu

Fig. 1

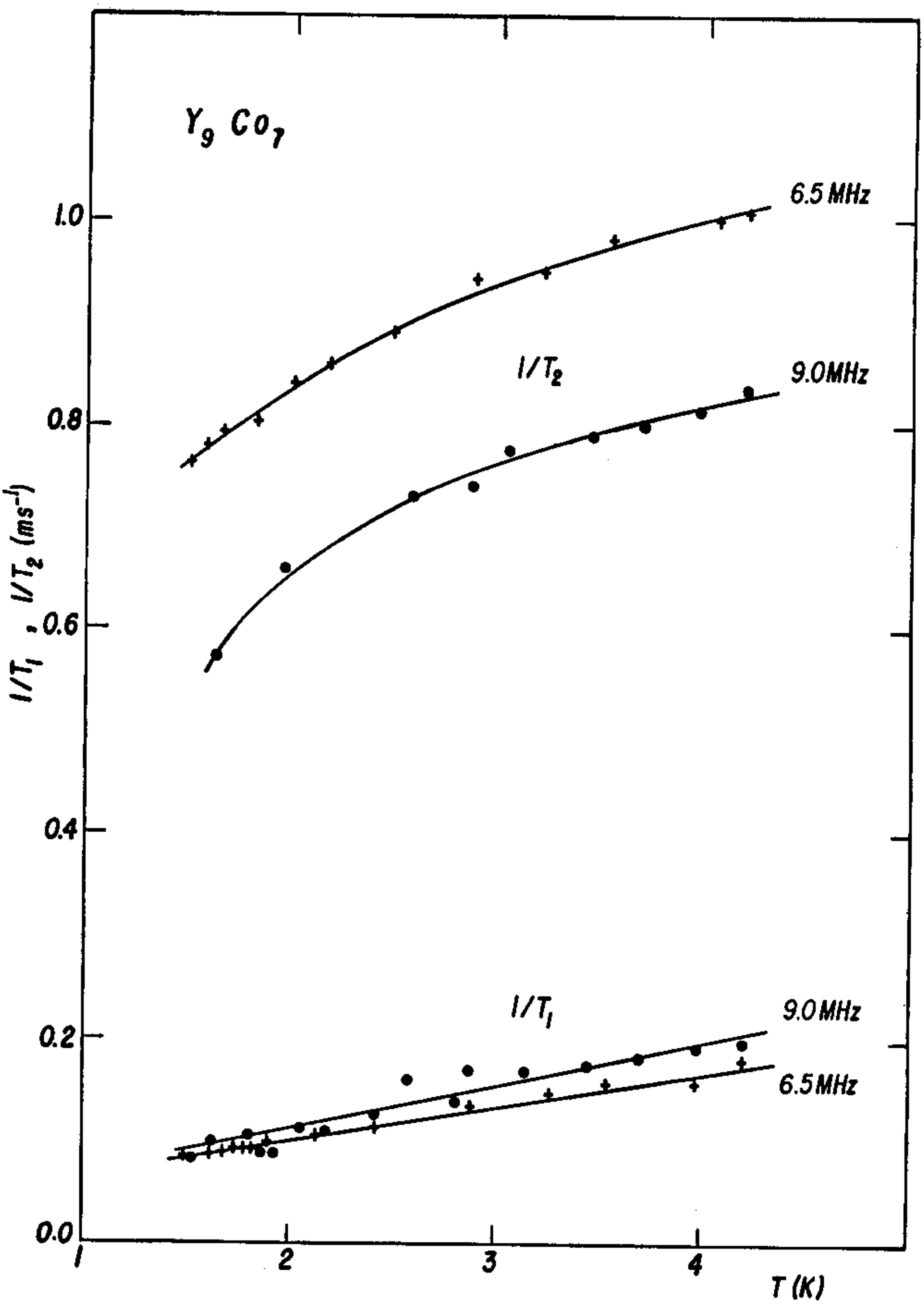
$Y_9\ Co_7$
6.5 MHz
$1/T_2$
9.0 MHz
$1/T_1$
9.0 MHz
6.5 MHz
$1/T_1$, $1/T_2$ (ms^{-1})
1.0
0.8
0.6
0.4
0.2
0.0
1
2
3
4
T (K)

Fig. 2

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