μSR studies on thermoelectric oxides

Jun Sugiyama [a,1], Jess H. Brewer [b], Eduardo J. Ansaldo [c], Hiroshi Itahara [a] Shingo Hirano [a] Toshihiko Tani [a]

[a] *Toyota Central R&D Labs. Inc., Nagakute, Aichi, 480-1192, Japan*
[b] *CIAR, University of British Columbia and TRIUMF, Vancouver, BC, Canada V6T 2A6*
[c] *University of Saskatchewan, Saskatoon, Saskatchewan, Canada S7N 0W0*

Abstract

To investigate the role of magnetism on transport properties of thermoelectric oxides, μSR spectroscopy has been used for polycrystalline $Ca_3Co_4O_9$, $Na_{0.7}CoO_2$ and $Sr_{0.92-y}Ca_yGd_{0.08}MnO_3$ samples in the temperature range between 300 and 2.5 K. It was found that $Ca_3Co_4O_9$ exhibits an incommensurate spin density wave transition around 100 K, though similar measurements on $Na_{0.7}CoO_2$ indicated no magnetic transitions below 250 K. The $Sr_{0.92-y}Ca_yGd_{0.08}MnO_3$ samples showed a ferro- or an antiferromagnetic transition below 250 K, while a muon precession was not observed even at 2.5 K probably due to an inhomogeneity of an internal magnetic field.

Key words: spin density wave; thermoelectrics; layered cobalt oxides; perovskite manganites

1. Introduction

Both p-type $Ca_3Co_4O_9$ [1,2] and n-type perovskite manganites $Sr_{1-x-y}Ca_yGd_xMnO_3$ [3] are known to exhibit large thermoelectric figure of merits ZT (the former's $ZT\sim$1 and the latter's $\sim$0.2 at 1000 K), for reasons currently unknown.

In these compounds, interactions between $3d$ electrons are considered to be strongly correlated with their 'good' thermoelectric properties. Since magnetism is also affected by such interactions, magnetic properties are worth to investigate to understand the mechanism of their thermoelectric properties.

A muon spin rotation and relaxation μSR is a powerful technique to detect local magnetic order and/or disorder in zero applied field; here, we report both weak-transverse-field (wTF-) μSR and zero-field (ZF-) μSR results on polycrystalline samples to know magnetism of these thermoelectric oxides.

[1] Corresponding author. Present address: Frontier Research Groups, Toyota Central R&D Labs., Nagakute, Aichi, 480-1192, Japan. E-mail: sugiyama@iclab.tytlabs.co.jp

2. Experimental

Polycrystalline samples of $Ca_3Co_4O_9$, $Na_{0.7}CoO_2$ $Sr_{0.92-y}Ca_yGd_{0.08}MnO_3$ were synthesized by a solid state reaction technique. The preparation and characterization of the samples were reported in elsewhere in detail [4]. The μSR experiments were performed on the M20 surface beam-line at TRIUMF. The experimental setup is described elsewhere [5].

3. Results and Discussion

3.1. *layered Co oxides*

According to the analyses of wTF-μSR spectra, $Ca_3Co_4O_9$ was found to exhibit a magnetic transition below $T_c^{\rm on}$ $\sim$100 K with a transition width of ΔT_c = 70 K [4]. Below $T_c^{\rm on}$, two types of relaxation were observed; one exhibits a fast relaxation rate on the order of 10 μs^{-1} and the other a slow one of about 0.1 μs^{-1}. Since wTF-μSR measurements on

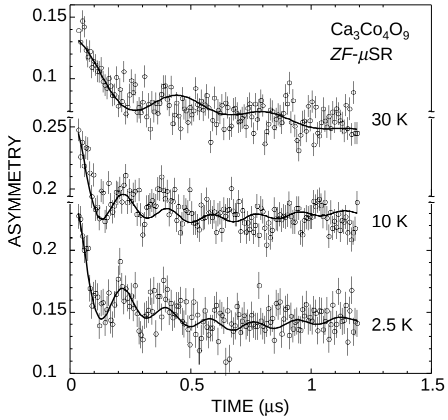

Fig. 1. *ZF*-μSR time spectra of $Ca_3Co_4O_9$ obtained at 30, 10 and 2.5 K; the bold lines represent the results of the fitting using the phenomenological function for the *IC-SDW* state.

$Na_{0.7}CoO_2$ indicated no magnetic transitions below 250 K, it is concluded that Co ions in the rocksalt-type [Ca_2CoO_3] subsystem in $Ca_3Co_4O_9$ are likely to play a dominant role in inducing the observed magnetic transition below ∼100 K.

Figure 1 shows *ZF*-μSR time spectra of $Ca_3Co_4O_9$ at 30, 10 and 2.5 K; a clear oscillation due to a quasi-static internal field is observed below 30 K. These spectra were fitted using the phenomenological function for the *IC-SDW* state, as in the case of the organic conductor $(TMTSF)_2X$ (TMTSF: tetramethyltetraselena-fulvalene, X=PF_6 NO_3 and ClO_4) [5]. The muon precession frequency ν_μ, which was obtained by the fitting, increases down to 10 K, then seems to be level off to a constant value of ∼55 MHz (see Fig. 2). Therefore, $Ca_3Co_4O_9$ was found to show a magnetic transition from a high-temperature paramagnetic state to a low-temperature *IC-SDW* state at T_{SDW}^{on} ∼100 K. The large transition width (∼70 K) is probably caused by randomness of the polycrystalline samples.

Since the resistivity-*vs.*-T curve exhibited a broad minimum around 80 K, the *SDW* transition was found to be associated with the change in the transport properties of $Ca_3Co_4O_9$.

3.2. *perovskite manganites*

Both resistivity and susceptibility measurements suggested that a low-temperature phase of $Sr_{0.92-y}Ca_y$ $Gd_{0.08}MnO_3$ changes from an antiferromagnetic phase to a ferromagnetic one around y∼0.6 with increasing y [3]. Nevertheless, *ZF*-μSR measurements of the samples with y=0.1 and 0.92 indicated no muon precessions even at 2.5 K. This suggests an inhomogeneous distribution of an internal magnetic field, probably due to a phase separation as proposed for $La_{1-x}Ca_xMnO_3$ [6].

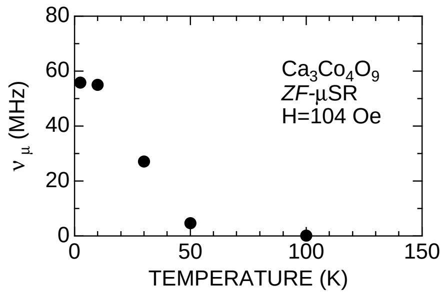

Fig. 2. Temperature dependence of the muon precession frequency ν_μ of $Ca_3Co_4O_9$.

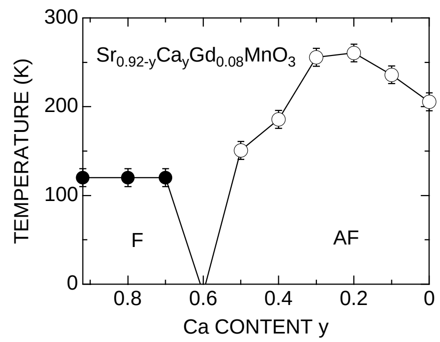

Fig. 3. magnetic phase diagram of $Sr_{0.92-y}Ca_yGd_{0.08}MnO_3$ determined by resistivity and susceptibility measurements.

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