NMR Studies of Co-Oxides with Large Thermoelectric Performance

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Abstract

The electronic state of Co-Oxides, $Na_{1+x}Co_2O_4$ and $Bi_{2-x}Pb_xSr_2Co_2O_y$ with large thermoelectric powers S and low resistivities ρ has been studied mainly ^{59}Co and ^{23}Na-NMR. In polycrystalline samples of $Na_{1+x}Co_2O_4$, effects of the Na atom rearrangement, which takes place with decreasing temperature T below ∼40 K, can be found in the T dependence of ρ and S. In $Bi_{2-x}Pb_xSr_2Co_2O_y$, the ferromagnetic order with the ordered moment of $\sim 0.1\mu_B$/Co has been found below ∼20 K in about a half volume of the sample with x ∼0.8. Even though the magnetically active parts often have a significant volume, its magnetism seems to be induced by lattice imperfections, and the electron system can be considered to be itinerant or Pauli paramagnetic.

Key words: $Na_{1+x}Co_2O_4$; $Bi_{2-x}Pb_xSr_2Co_2O_y$; NMR; Thermoelectric power; Resistivity

The large thermoelectric powers S of several Co oxides such as $Na_{1+x}Co_2O_4$, $Bi_{2-x}Pb_xSr_2Co_2O_y$ and $Ca_3Co_4O_9$ seem to be rather unusual, because their electrical resistivities ρ are very small. Koshibae *et al.* [1] have discussed possible origins of the large thermoelectric powers of Co oxides by using the Heikes formula, which can be applied to systems with very narrow electron band or with strongly correlated electrons. Here, to investigate whether these Co oxides really have strongly correlated electrons, we have performed ^{59}Co-NMR. For $Na_{1+x}Co_2O_4$, ^{23}Na-NMR has also been carried out.

Samples used here were prepared by proper solid reaction. For $Na_{1+x}Co_2O_4$, the heat treatment is performed as described in Ref. [2]. The samples were confirmed to be the single phase by X-ray diffraction. For these samples, magnetic susceptibilities χ, ρ and S were measured in the temperature (T) range between 5 K and 300 K. The NMR spectra were obtained by recording the spin echo intensities with the frequency or the magnetic field being changed step by step.

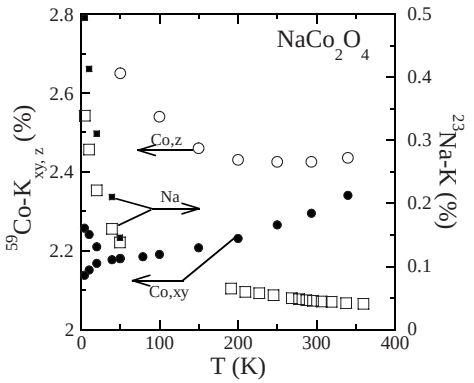

Fig. 1. ^{59}Co and ^{23}Na NMR Knight shifts are plotted against temperature T. The x or y directions are parallel to the CoO_2 planes. The anisotropies of ^{23}Na shifts are much smaller than that of ^{59}Co shifts.

The ^{59}Co-NMR spectra observed for the samples of $Na_{1+x}Co_2O_4$ with x=0 and 0.5 consist, for unknown reasons, of two components with different quadrupole frequencies ν_Q. The ^{59}Co-NMR Knight shifts (^{59}K) of these components are almost equal above ∼40 K. Below this temperature, the difference between these shifts becomes significant with decreasing T, as can

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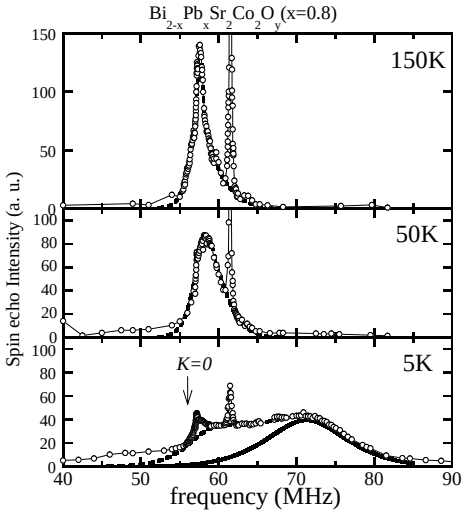

Fig. 2. ^{59}Co NMR spectra of Bi1.2Pb0.8Sr2Co2Oy are shown against the frequency at 150 K (Top), 50 K (middle) and 5 K (bottom). The dotted lines indicate the spectra of main phases. The thick solid line shows the new spectra which appear which the magnetic order at $\sim$ 20 K.

be realized from the different T-dependences of their shifts $^{59}K_{\rm xy}$ shown in Fig.1. The ^{23}Na-NMR spectra also have two components, corresponding to two crystallographically distinct sites. In the T region below 40 K, the $\nu_{\rm Q}$-distribution of one component gradually becomes broader with decreasing T, while the distribution of another one seems not to depend on T. The shifts(^{23}K) also seem to have slightly different T dependences below $\sim$40 K, while the almost same T dependences are observed above $\sim$40 K. The present observation of the $\nu_{\rm Q}$-broadening for one component indicates the gradual rearrangement of the Na atoms at the corresponding sites below $\sim$40 K, which induces the inhomogeneous charge distribution. The anomalous decrease of ρ and S observed below $\sim$40 K with decreasing T seems to be caused by this gradual rearrangement of the Na atoms. The rearrangement may also be an origin of the increase of the difference between the $^{59}K_{\rm xy}$ values observed below $\sim$40 K with decreasing T.

Recent works on $NaCo_{2-x}Cu_xO_4$ [3] or $Na_{1.5}Co_2O_4$ [4] found the specific heat anomaly at $\sim$22 K which indicates the existence of certain kind of phase transition. However, we have not observed such kind of anomaly for the present samples, even though the accuracy of the measurements is good enough to observe the reported magnitude of the anomaly. Then, the abovementioned transport anomalies below $\sim$40 K cannot be considered to be due to the reported phase transition.

The isotropic part of the Knight shift $^{59}K_{\rm iso} \equiv (2K_{\rm xy}+K_{\rm z})/3$ of $Na_{1+x}Co_2O_4$ exhibits only weak T-dependence, while ^{23}K and $^{59}K_{\rm ani}$ $(=(2K_{\rm z}\text{-}2K_{\rm xy})/3)$ have significant T dependence and seem to follow the T dependence of χ. The similar result have also been obtained for $Bi_{2-x}Pb_xSr_2Co_2O_y$. The results can be understood as follows. The T-independent $^{59}K_{\rm iso}$ indicates that these Co oxides commonly have itinerant electron system with Pauli paramagnetic behavior. On the other hand, the dipole field of local moments around lattice imperfections within the CoO_2 layers induces the T-dependent behavior of ^{23}K and $^{59}K_{\rm ani}$. The magnetically active parts around the localized moments also contribute to their T-dependent behavior. Note that the dipole field does not contribute to $^{59}K_{\rm iso}$ and also that impurity phases which may exist in the samples do not induce the observed T dependent behavior of $^{59}K_{\rm ani}$ and ^{23}K of the main phase.

In Fig. 2, the ^{59}Co-NMR spectra of the sample of $Bi_{2-x}Pb_xSr_2Co_2O_y$ with $x \sim 0.8$ are shown, where the T-dependence of the peak position and the spectral shape are not very significant above 20 K. With decreasing T, however, new spectra appear at $\sim$20 K along with the magnetic transition, which has also been observed in the M-H curves. Because the newly observed spectra shown by the thick solid curve in the bottom panel of Fig. 2, are located at the frequency higher than the position of the peak observed at high temperatures, the system can be considered to be ferromagnetic below $\sim$20 K. The spontaneous magnetization is estimated to be $\sim$0.1 $\mu_{\rm B}$/Co at 5 K by assuming that the hyperfine field is the same as that of La_2CoO_4. The value is consistent with the previously reported one [5]. Because the ordered moment is small and the transition seems to be rather smeared out, it is presumed that the transition is due to the ordering of moments induced around lattice imperfections.

In summary, $Na_{1+x}Co_2O_4$ and $Bi_{2-x}Pb_xSr_2Co_2O_y$ have been revealed to basically exhibit Pauli paramagnetic behavior. However, the fact that the magnetically active parts are easily formed possibly by lattice imperfections indicates that their electrons are located near the region of the strongly correlated system.

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