

Cold neutron inelastic scattering study for Co-121 and related cobaltites

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Cold neutron, $\lambda = 4.22 \text{ \AA}$, inelastic scattering experiment was carried out for the thermoelectric oxides Co-121, i.e. $[\text{Ca}_2\text{CoO}_3]_{0.62}[\text{CoO}_2]$, and related cobalt oxides by the use of a TOF-type multicounter cold neutron spectrometer, AGNES, in JAERI. Polycrystalline samples were used for the experiment at 12K, 30K, 90K and room temperature. Low energy inelastic intensities, being $\Delta E < 3 \text{ meV}$, are observed in the Co-121 in which $\Delta E = 1.7 \pm 0.2 \text{ meV}$ peak is observed at room temperature. This peak becomes broad at 90K, 30K and 12K, being stronger at 12K. Since the paramagnetic to ferromagnetic phase transition at 27K was previously found with decreasing temperature from μ SR measurement by Sugiyama et al.[1], above low energy excitation could be discussed in terms of the spin ordering of Co^{4+} ions or localized motion of displaced oxygen atoms.

Keywords: Cobalt oxide, thermo electric semiconductor, magnetic ordering, neutron scattering

1. INTRODUCTION

Strongly correlated $3d^5$ or $3d^6$ electrons of Co^{4+} and Co^{3+} ions, respectively, situated in the triangular CdI_2 -type CoO_2 layers has attracted much attentions because of the semiconducting and, some times, superconducting behaviors below 4.2K[2]. High Seebeck coefficient and low electrical resistivity were reported for Na_xCoO_2 with $x=0.7$ [3] and Co-121, i.e. $[\text{Ca}_2\text{CoO}_3]_{0.62}\text{CoO}_2$ and identified as Ca349 some times[4], being typical thermoelectric oxide semiconductors. Significant thermoelectric properties, i.e. high Seebeck and Peltier coefficient, of these oxides at temperatures in the range from the ambient to about 1000K were analyzed using Heikes formula[5] by Koshibae et al. [6] in terms of the spin entropy flow due to the charge flow activated by the thermal flux. The Seebeck coefficient at elevated temperature was estimated from the concentration of Co^{4+} ions which have the six-fold multiplicity of spin ordering with $S=1/2$ at three t_{2g} orbitals, namely, xy , yz and zx orbitals. The estimated values have been reasonably agreed with the experimental ones. It means that the magnetic ordering in the cobalt-oxygen layer has a key factor for the high thermoelectric properties realized in the Co-121 and related cobalt oxide semiconductors. It has been reported based on the magnetic measurement[7] and the μ -SR spectra[1] by Sugiyama that the Co-121 undergoes a paramagnetic to ferromagnetic or weak ferromagnetic SDW phase transition at about 27K. The 27K transition has also been noticed from the electrical

resistance by Miyazaki et al.[4] Since such magnetic transition is not reported among other cobalt oxide semiconductors, it was expected that this transition takes place in the rocksalt-type block layer rather than the CoO_2 conduction layers of the Co-121. Sugiyama et al.[1] proposed three phase transition temperatures at about 27K, 100K and 600K or above which correspond, respectively, to the long-range-spin ordered phase(LRO) to the short-range ordered one(SRO), SRO to the metallic paramagnetic phase(PM) and PM to the semiconducting paramagnetic(PM) phase with increasing temperature. Based on the single crystal runs, he determined the spin orientation in the LRO phase, $T=4.2\text{K}$, normal to the CoO_2 layer from the direction which exhibits the Larmor precession in the μ SR spectrum.

Figure 1 schematically shows the crystal structure of the Co-121.

For better understanding of the high thermoelectric performance of the Co-121 and related cobaltites, it has been needed to elucidate temperature dependent behaviors of magnons and phonons of these crystal systems in the low temperature range below and over 27K by the neutron inelastic scattering measurement. It was expected that low energy local mode could exist below 3meV in the magnetically ordered clusters as in the case of manganites[8]. In the $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ system with x being less than 0.2, present authors observed 1.2meV almost flat, dispersion less, excitation in the low temperature

ferromagnetic metallic regime.

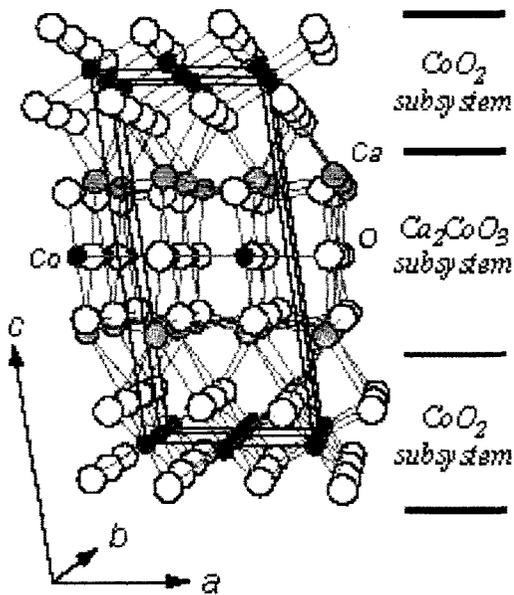


Fig.1 Fundamental cell of the monoclinic Co-121, which is the (3+1)-dimensional lattice[4]. Two subsystems, Ca_2CoO_3 and CoO_2 , systems are connecting incommensurate way, in the ratio about 0.62/1.0 parallel to the b-axis.

2. EXPERIMENTAL PROCEDURE

Neutron inelastic scattering measurement was carried out for the Co-121 and related cobalt oxides, (Cu,Co)-221, i.e., $[\text{Ca}_2(\text{Co}_{0.65}\text{Cu}_{0.35})_2\text{O}_4]_{0.624}\text{CoO}_2$, and Co_3O_4 by the use of a cold neutron spectrometer, AGNES[9], installed in the JRR-3M reactor guide-hall of Japan Atomic Energy Research Institute.

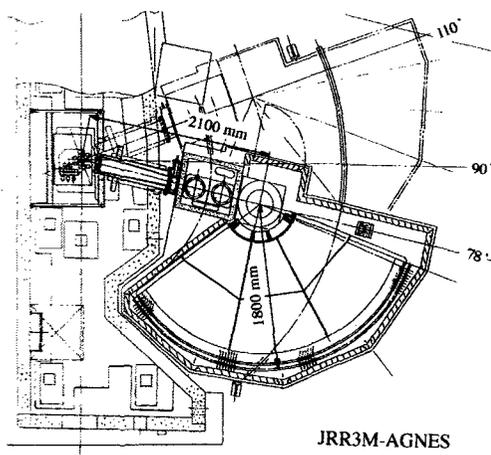


Fig.2 Layout of a cold neutron spectrometer AGNES. This apparatus has been installed at the cold neutron guide tube, C3, in the guide-hall of JRR-3M. The energy value of the scattered neutron is determined by the time-of-flight

method. The energy resolution is about 0.1meV in the present experimental condition.

Figure 2 shows a top view of the apparatus. Co_3O_4 powder was selected as a reference sample which might not show anomalous magnetic excitations. Cold neutron with the wave length, $\lambda = 4.22 \text{ \AA}$, was used through out the experiment. Cold neutron scattering experiment was carried out at 12, 30, 90K and room temperature for the Co-121 sample. The same experiment for the reference samples, i.e., $\gamma\text{-Na}_{0.7}\text{CoO}_2$, (Cu,Co)-221 and Co_3O_4 were only done at room temperature. Powder cobaltite samples were synthesized by the solid state reaction method as described elsewhere[3,4]. The data acquisition time for each sample was about 48 hours.

3. RESULTS

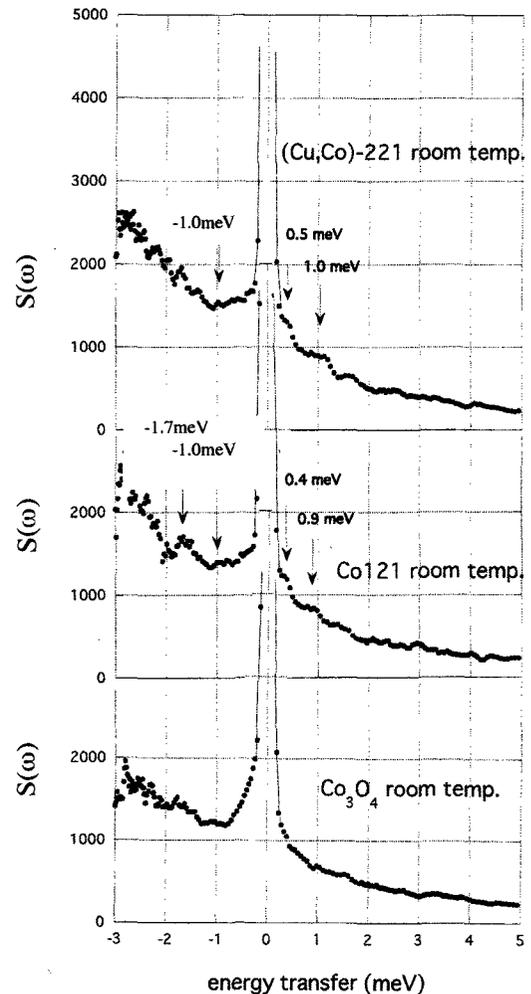


Fig.3 Cold neutron scattering intensity, $S(\omega)$, of the (Cu,Co)-221, Co-121 and Co_3O_4 at room temperature. The horizontal axis corresponds to the energy transfer values of the incidence. The negative side of the spectra corresponds to the kinetic energy loss side, i.e. the Stokes side. The central peaks are the elastic scattering components.

Figure 3 represents observed cold neutron scattering intensities, $S(\omega)$, i.e., the summation of $S(\mathbf{q},\omega)$ in the q -space, of the (Cu,Co)-221, Co-121 and Co_3O_4 , while ω is the angular frequency, $2\pi\nu$.

There are low energy small peaks in the (Cu,Co)-221 and Co-121. The Co-121 clearly shows an inelastic scattering peak at -1.7meV. In the energy-gain side, right hand side from the central peak, there are at least two steps or peaks at about 0.5 and 1.0meV in the (Cu,Co)-221 and Co-121 either.

Figure 4 shows temperature dependent change of the inelastic intensities of the Co-121

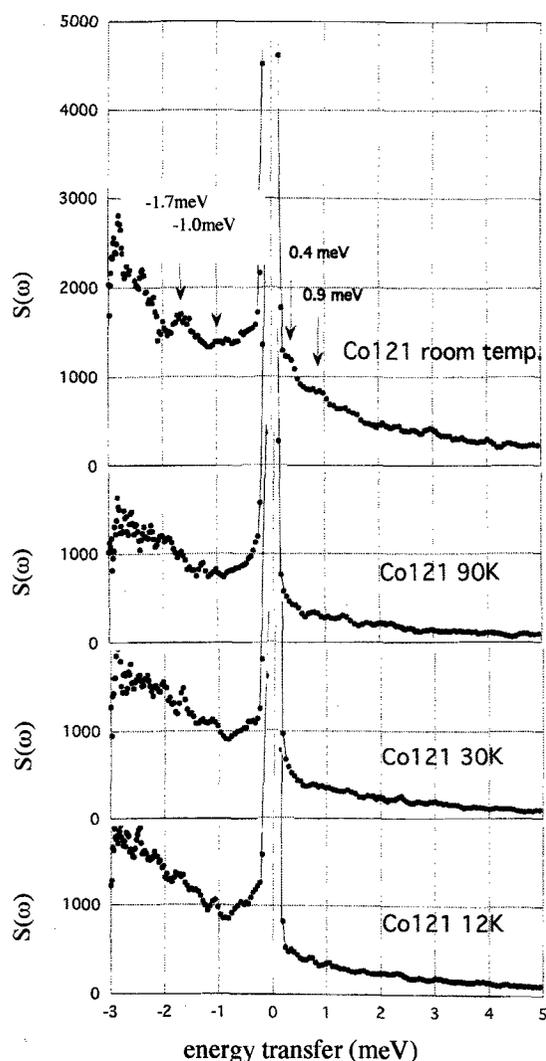


Fig.4 Temperature dependent change of the spectra of the Co-121. The measurements were performed in the LRO (12K), SRO (30K and 90K) and PM metallic phase regime (RT), respectively.

The -1.7meV peak seems to move to the left and made broad intensities at 90, 30 and 12K, being broader and

higher at 12K. If we could compare the scattering intensity distribution of Co_3O_4 in Fig.3, it can be noticed that relatively high inelastic scattering intensities exist in the range from -1 to -3meV in the Co-121.

The small steps or peaks appeared in the energy gain side, the excitation annihilation, a^- , side at room temperature, disappeared at low temperatures. Disappearance of the steps or peaks corresponds to the smearing of the responsible excitations at low temperature range, and those are the Bose particles.

4. DISCUSSION

Several small inelastic scattering peaks have been found for the first time in the Co-121 and (Cu,Co)-221 at room temperature. The -1.7meV peak, corresponding to the creation of 1.7meV excitation, found in the Co-121 may be connected with the creation of localized magnon mode as in the cases of doped manganite [8,10,11]. It is also conceivable that its broadening corresponds to the creation of magnon branch in the LRO phase stabilized at low temperature range.

One of the significant nature of the crystal structures of (Cu,Co)-221 and Co-121 is their incommensurated but periodic displacements of the constituent atoms, especially oxygen atoms in the block layers. It is natural to assume that locally displaced light atoms, i.e., oxygen atoms in these crystals, could locally vibrate in the high temperature range. There are two other possible explanations for the low energy excitation peaks below 2meV, i.e., localized magnetic excitations in the SRO particles or tunneling motions, $\pm\omega$ and $\pm 2\omega$, of trapped light atoms, e.g., H^+ . The low energy peaks in the doped manganites were due to the former one. If the latter one would be the case, observed temperature dependent increase of the peaks could not be answered.

5. CONCLUSION

There are low energy excitation peaks at about +0.4, ± 0.9 or ± 1.0 and -1.7meV and below in the Co-121 thermoelectric semiconductor. -1.7meV peak were broadened in the low temperature range but other peaks were disappeared there, where the LRO or SRO phases are stable. Similar low energy peaks are observed in the (Cu,Co)-221 at room temperature. These excitations in the energy gain side, anti-Stokes side, are due to the Bose particles, and conceivably correspond to the local vibrations of incommensurately displaced oxygen atoms.

ACKNOWLEDGEMENT

Present study was partly supported by the Aid of JST-CREST (Fujishima program) and JSPS Grant "Kiban"

A(2) 14205095.

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(Received December 23, 2004; Accepted February 15, 2005)