

Static and Dynamic Corrugation of Thermoelectric Cobaltites

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Abstract Structural characteristics of the high performance cobaltite thermoelectric semiconductors have been studied intensively by means of X-ray and neutron diffraction measurements and high resolution electron microscopy (HREM). These cobaltites consist of CoO₂ triangular conducting sheets and several different types of block layers, i.e., Na, Ca, Sr single layers, three or four layered rock-salt layers, where Co-O₂ square lattices are situated at their middle, and Bi-O or Ti-O double layers plus alkaline oxygen layers. Cold neutron scattering technique is employed to search possible low-energy excitation modes, being unique for nearly 1D and 2D crystals, and phonon density of states, DOS, of several high performance cobaltites at temperatures in the range from 10K to the ambient. Low energy, i.e., less than 2meV, excitation modes were found in the three different thermoelectric ceramics, i.e., γ -Na_{0.7}CoO₂, [Ca₂CoO₃]_pCoO₂, and [Ca₂(Cu,Co)₂O₄]_pCoO₂. Possible origin of these low energy excitations are discussed in terms of low-energy corrugation mode generated due to weak chemical bondings, for which Van-der-Waals force dominates, between the CoO₂ conduction sheets. These characteristics could be the key to realize low thermal conductivity and high-ZT of these ceramics.

Keywords: Neutron scattering, Thermoelectrics, Thermoelectric semiconductor, Cobalt oxide, Na_{0.7}CoO₂, Co-121, Ca349, corrugation mode

Introduction

Strongly correlated 3d⁵ or 3d⁶ electrons of Co⁴⁺ and Co³⁺ ions, respectively, situated in the triangular CdI₂-type CoO₂ layers has attracted much attention because of the semiconducting and, some times, superconducting behaviors below 4.2K [1]. High Seebeck coefficient and low electrical resistivity were reported for Na_xCoO₂ with x=0.7 [2] and Co-121, i.e., [Ca₂CoO₃]_{0.62}CoO₂ being identified as Ca349 some times [3], 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 [4] by Koshibae et al. [5] 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 Co⁴⁺ 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 [6] and the μ -SR spectra [7] 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. [3]. Since such magnetic transition is not reported among other cobalt oxide semiconductors, it was expected that this transition takes place in the rock-salt-type block layer rather than the CoO₂ conduction layers of the Co-121. Sugiyama et al. [7] 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=4.2K, normal to the CoO₂ layer from the direction which exhibits the Larmor precession in the mSR spectrum.

For our better understandings of the high thermoelectric performance of the γ -Na_xCoO₂, Co-121 and related cobaltites, it has been needed to elucidate temperature

dependent behaviors of magnon and phonon spectra of these crystal systems in the low energy transfer range 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[8,9]. 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. Low energy phonon mode was also the possibility.

Experimental Procedure

Neutron inelastic scattering measurement was carried out for the $\gamma\text{-Na}_{0.7}\text{CoO}_2$ and related cobalt oxides, Co-121, i.e., $[\text{Ca}_2\text{CoO}_3]_{0.62}\text{CoO}_2$, and Co_3O_4 by the use of a cold neutron spectrometer, AGNES[10], installed in the JRR-3M reactor guide-hall of Japan Atomic Energy Research Institute. 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.

Co_3O_4 powder was selected as a reference sample which might not show anomalous excitations. Cold neutron with the wave length, $\lambda = 4.22 \text{ \AA}$, was used throughout the experiment. Cold neutron scattering experiment was carried out in the range from 10K to the ambient. The same experiment for the reference sample, Co_3O_4 , was only done at room temperature. Powder cobaltite samples were synthesized by the solid state reaction method as described elsewhere[2,3]. The data acquisition time for each sample was about 46-48 hours. The energy transfer value ΔE corresponds to the kinetic energy loss or gain of the incident neutrons. The cold neutron scattering experiment was carried out in the energy and momentum transfer ranges of $-3.2\text{meV} < \Delta E < 100\text{meV}$ and $0.26 \text{ \AA}^{-1} < \Delta Q < 2.72 \text{ \AA}^{-1}$, respectively.

Experimental results

Figure 1 represents observed cold neutron scattering intensities, $S(\omega)$, i.e., the summation of $S(\mathbf{q},\omega)$ in the Q -space, of the $\gamma\text{-Na}_{0.7}\text{CoO}_2$, Co-121 and Co_3O_4 , while ω is the angular frequency, $2\pi\nu$.

There are low energy small peaks in the $\gamma\text{-Na}_{0.7}\text{CoO}_2$. However, there is no such peak in the Co_3O_4 which has cubic Spinel structure. Low energy inelastic peaks were previously observed in the thermoelectric materials such as $\text{Ba}_{0.1}\text{CoSb}_3$ [12]. The origin of the excitations was discussed in terms of the local lattice vibration modes related with the "rattling" motions of the heavy "rattlers". Since the inelastic

peaks are due to the vibration modes of the atoms which have large incoherent cross sections, σ_{inc} , relative the other atoms in the samples, it is easily assumed that the small peaks are due to the vibrations of cobalt atoms for which $\sigma_{\text{inc}} = 4.8 \times 10^{-24} \text{ cm}^2$ while σ_{inc} of Na, Ca, Sr and O are small, i.e., 1.62, 0.05, 0.06 and $0.0 \times 10^{-24} \text{ cm}^2$, respectively.

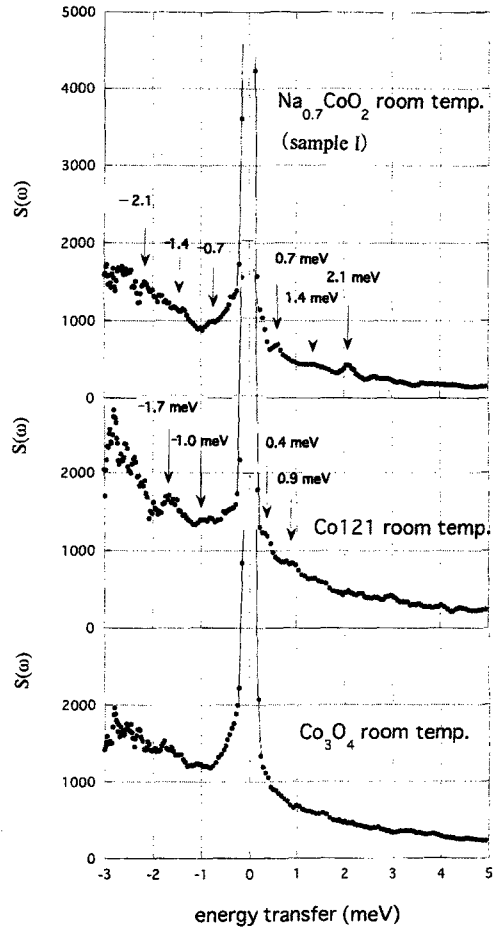


Fig.1 $S(\omega)$ curves of three cobaltites.

Coherent phonon scatterings and diffuse multiphonon scattering exist in the low energy transfer range. The phonon branch peaks are possible to observe for the large single crystal runs but that kind of peaks are not easy to observe for the powder samples because normal phonon dispersion curves have strong energy vs. wave-number relationships. The multiphonon scattering becomes weak at low temperature range because its strong temperature dependency.

Figure 2 shows observed phonon density curves calculated from the $S(\omega)$ curves of two different $\gamma\text{-Na}_{0.7}\text{CoO}_2$ samples. There are two large DOS peaks, i.e., acoustic and optic normal phonon DOSs at about 20 and

70meV, respectively.

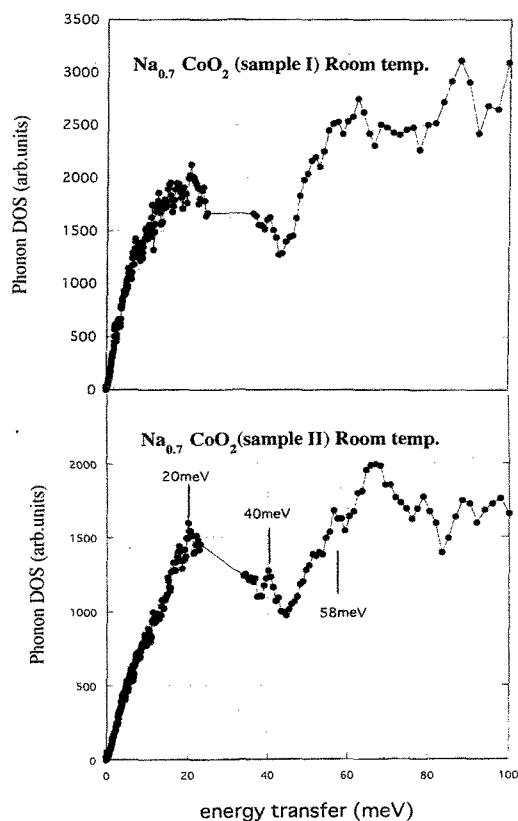


Fig.2 Phonon DOS of two γ - $\text{Na}_{0.7}\text{CoO}_2$

There are some differences in the two curves but two curves have qualitative identity, i.e., the first hump is seen in the range $\Delta E < 40\text{meV}$ and the next one with $\Delta E > 40\text{meV}$. The DOS curves in the range of $22\text{meV} < \Delta E < 35\text{meV}$ was excluded since the scattering intensities in that range are mainly due to those of the incident $\lambda/2$ component. There are at least three sharp peaks or shoulders at 20, 40 and 58 meV in both curves. These ones could be the indications of the weakly Q -dependent phonon-dispersion relationship of particular modes, conceivably running parallel to the CoO_2 plane.

Figure 3 represents temperature dependent change of $S(\omega)$ curve of γ - $\text{Na}_{0.7}\text{CoO}_2$ (sample II). At room temperature, the $S(\omega)$ curve show some difference between the sample I shown in Fig.3 but 2.1meV peaks are commonly seen in both samples. $\pm 0.7\text{meV}$ peaks in the sample I may have the correspondence between the -1.1meV and 1.0meV peaks in the sample II. -1.1meV peak has almost no temperature dependent

change but -2.1meV peak disappeared or shifted to $\rightarrow 2.8\text{meV}$ at 10K.

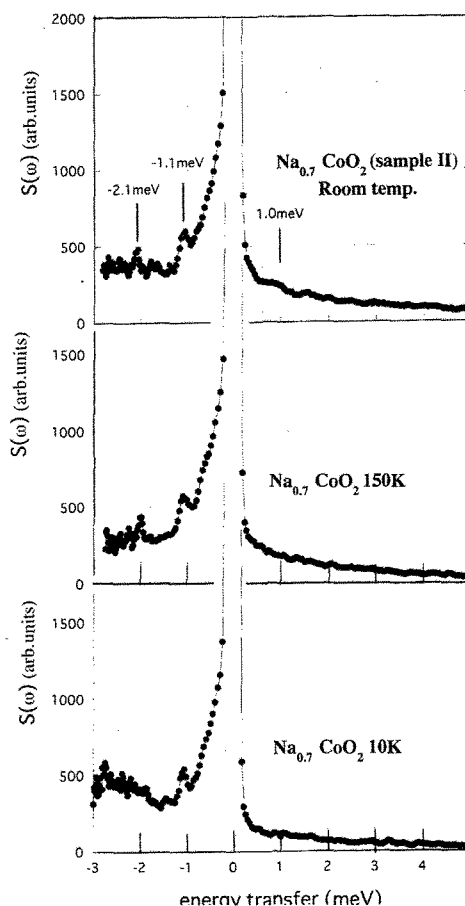


Fig.3 Temperature dependent change of $S(\omega)$ curves of γ - $\text{Na}_{0.7}\text{CoO}_2$ (sample II).

change but -2.1meV peak disappeared or shifted to -2.8meV at 10K.

Static and dynamic corrugation

Figure 4 shows filtered HREM images of a thermoelectric oxide $[\text{Bi}_{1.79}\text{Sr}_{1.98}\text{O}_y]_{0.63}[\text{RhO}_2]$ reported by Yubuta et al.[13]. This oxide has almost isomorphous structure of the cobaltite counterpart. Two types of static modulation modes are typically represented in Fig.4(a) and 4(b), in which chemical ordering, possibly CDW, in the block layers and displacement modulation perpendicular to the ab -plane are exhibited, respectively. Both modulation waves have incommensurate wave lengths relative to the RhO_2 and $\text{Bi}_2\text{Sr}_2\text{O}_x$ layers. Because of the periodic vertical displacement of BiO_2 double layers, observed modulation

in the BiO_2 double layers can be described in terms of the static corrugation which is frequently reported in the “clay” kind minerals, superconducting perovskites and related oxides[14].

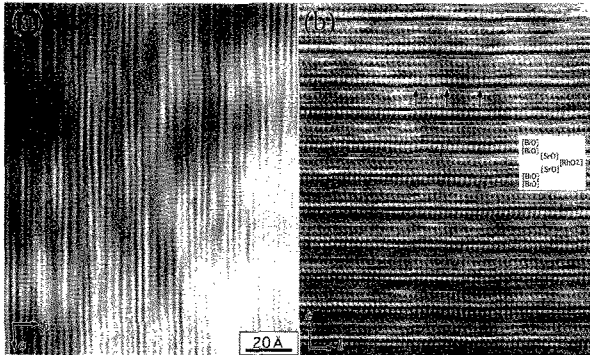


Fig. 4 Fourier-filtered high-resolution image of a thermoelectric oxide $[\text{Bi}_{1.79}\text{Sr}_{1.98}\text{O}_y]_{0.63}[\text{RhO}_2]$ taken with the incident electron beam parallel to (a) c -axes and (b) a -axes.

The static corrugation occurs due to weak chemical bonds between the corrugated layers and the rest of the crystal blocks[15].

The transverse phonon modes, i.e., T -modes, propagate parallel to the ab -plane have two “normal” branches, T_x and T_y , and a soft mode, T_z . The soft mode is due to the vertical shear deformation of the CoO_2 layers and the energy of the T_z mode is ~ 0.3 or less than those of the other two shear modes, T_x and T_y , which are the dynamical shearing deformations in the x - and y -directions, respectively. It is easily expected that the T_z phonon mode has its partial DOS peak at about 6 meV which is the energy of the 0.3 of the 20 meV DOS peak position, which is conceivably the L -mode peak. Mixed valence states, i.e., Co^{3+} and Co^{4+} states, of cobalt ions in the CdI_2 layers is one of the unique characteristics of the thermoelectric cobaltites. Due to above, the phonon dispersion curves are folded into a narrow Brillouin zone boundaries which are divided from the original one. The 6 meV peak could shift down in a range from 3 to 4 meV by the ordered arrangement of Co^{4+} ions and local variation of “spring constants” due to that. These energy values are suitable for the T_z

mode peak. We may call these “pin-downed” T_z modes as “pin-downed dynamical corrugation modes” in the CoO_2 layer. It is easily expected that observed low energy excitation peaks in the energy range lower than 3meV could have close relationship with these “pin-downed dynamical corrugation modes”.

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