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Metal-nonmetal transition in Li_xCoO_2 thin films and thermopower enhancement at high Li concentration

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We investigate the transport properties of Li_xCoO_2 thin films whose resistivities are nearly an order of magnitude lower than those of the bulk polycrystals. A metal-nonmetal transition occurs at $x \sim 0.8$ in a biphasic domain and the Seebeck coefficient (S) is drastically increased at ~ 140 K($\equiv T^*$) with increasing the Li concentration to show a peak of magnitude ~ 120 μV/K in the S-T curve of $x = 0.87$. We show that T^* corresponds to a crossover temperature in the conduction, most likely reflecting the correlation-induced temperature dependence in the low-energy excitations.

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Thermoelectric (TE) energy conversion is one of the key technologies for energy savings and environmental protection. There has been an extensive quest over decades for materials exhibiting higher TE figure of merit $ZT = S^2T/\rho\kappa$, where S, T, ρ, and κ are the Seebeck coefficient, absolute temperature, resistivity, and thermal conductivity, respectively.[1] Band theory of solids predicts that heavily doped semiconductors having carrier concentrations $n \sim 10^{19}$ cm^{-3} are candidates for high-ZT materials but metallic materials are not.[1] Therefore, the fairly large S (~ 100 μV/K at 300 K) in Na_xCoO_2 showing metallic ρ with $n \gtrsim 10^{21}$ cm^{-3} (Ref. 2) has attracted much attention for its origin[3–11] and also has triggered the search for metallic TE materials having CoO_2 layers as common building blocks.[12–18] Na_xCoO_2 was further revealed to exhibit unconventional superconductivity,[19] charge[20] and Na-ion orderings,[21] and three-dimensonal magnetism.[22,23] Electronically, A-ion removal from A_xCoO_2 (A: alkaline or alkaline-earth metal) creates holes in the valence band. It has been debated how far band theory can explain the largeness of S (Refs. 3, 9, and 10) and how far strong correlations can be relevant.[4–8,11] Recently, Lee *et al.*[13] reported that S is further increased in Na_xCoO_2 at $x > 0.75$, and that the S-T curve shows a peculiar peak of magnitude ~ 350 μV/K at ~ 100 K, indicating that Na_xCoO_2 in the high-x region may serve as an efficient hole-type TE material, although the origin of the increase in S at high x is also not clear partly because Na ions are unstable and mobile at ambient temperatures.[21,24,25]

Li_xCoO_2 (Refs. 26 and 27) has a layered structure similar to Na_xCoO_2, and is the most common cathode material for Li rechargeable batteries since Li ions can be removed from and inserted into Li_xCoO_2 repeatedly through an electrochemical method at ambient temperatures.[28,29] There has been many studies on the relationship between the structure and the Li-ion diffusion properties as reviewed by Antolini,[30] and also on the magnetic properties.[31–35] In addition, Li_xCoO_2 is known to exhibit fairly large S (Refs. 36–38) comparable to that of Na_xCoO_2. Even though ρ of the polycrystalline samples are rather high due to the grain boundaries, there is a signature of electron delocalization upon Li deintercalation,[37,38] indicating that Li_xCoO_2 is a potentially metallic TE material. Herein, we report transport properties of Li_xCoO_2 epitaxial thin films whose resistivities are nearly an order of magnitude lower than those of the polycrystalline samples. We observe a metal-nonmetal transition at $x \sim 0.8$ and an increase in S with increasing x that results into a peak in the S-T curve at high Li concentration. We present a picture that the electronic transport of Li_xCoO_2 at high x is strongly affected by both disorder and electron correlations.

In order to obtain the Li_xCoO_2 epitaxial thin films, we first grew epitaxial films of $Na_{0.8}CoO_2$ on the (111) face of yttria stabilized zirconia (YSZ) substrates by the reactive solid-phase epitaxy method.[39–41] The $Na_{0.8}CoO_2$ epitaxial thin films thus obtained were converted into $Li_{0.92}CoO_2$ thin films by treating them in $LiNO_3$/LiCl salt at 260 °C for 4 h in an Ar atmosphere. During the topotactic ion-exchange treatment, the epitaxial relation of the film and the YSZ substrate was preserved [the in-plane and out-of-plane x-ray diffraction (XRD) patterns show sharp peaks of the films and the substrate simultaneously; see Fig. 1(a)], and the grain size of ~ 0.5 μm was virtually unchanged, thanks to the lateral ion diffusion during the ion exchange making less impact on the crystallinity of the CoO_2 layers.[39–41] Then the Li ions were subtracted by immersing the $Li_{0.92}CoO_2$ thin film in $K_2S_2O_8$ aqueous solution (0.03 mol/l) at room temperature. The Li concentrations were controlled by the immersing time and x was estimated from the 0003 XRD peak [Fig. 1(b)] using the relationship between x and the lattice parameter of the bulk.[39,42,43] The thin films for $0.75 \leq x \leq 0.87$ was separated into Li-rich and Li-poor phases, whereas those for $x \leq 0.70$ and $0.92 \leq x$ were in a single phase. A two-phase coexistence was also reported in the polycrystalline samples at $0.75 \leq x \leq 0.95$ (Refs. 30 and 42) so that the thin films investigated herein had structural properties similar to the bulk. ρ was recorded by a dc four-probe method under van der Pauw configuration and S was recorded by applying temperature difference of <3 K in the in-plane direction. Temperature-dependent hysteresis was not observed in the transport measurements. Typical thickness of the films was ~ 60 nm.

Figure 2(a) shows ρ-T curves of the Li_xCoO_2 epitaxial films. The $x = 0.66$ sample shows positive $\partial\rho/\partial T$ at

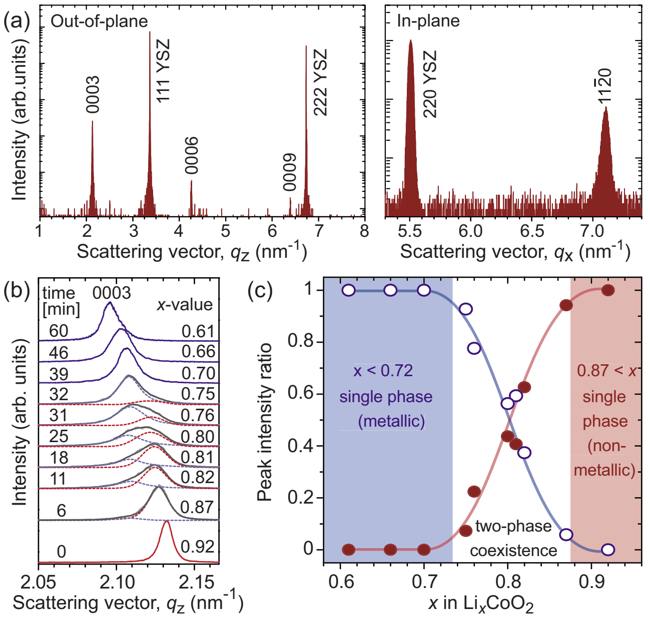

FIG. 1. (Color online) XRD patterns of Li_xCoO_2 thin films. (a) Out-of-plane (left) and in-plane (right) XRD patterns of $Li_{0.92}CoO_2$ epitaxial thin film. (b) 0003 peaks of Li_xCoO_2 thin films. With increasing the immersing time, the z component of the scattering vector is decreased, from which we deduced the Li concentration x. Phase separation is observed for the samples $0.75 \leq x \leq 0.87$, in which the 0003 peak can be deconvoluted into two components [red (gray) dashed curve: a peak originating from the high Li concentration phase; blue (light gray) dashed curve: a peak originating from the low Li concentration phase]. (c) Ratios of the high (filled circle) and the low (empty circle) Li concentration phases deduced from the 0003 peak analysis shown in (b).

$T \lesssim 240$ K, indicating that the single phase samples for $x \leq 0.70$ is metallic at low T. With increasing x, ρ is increased, and a metal-nonmetal transition occurs at $x \sim 0.8 (\equiv x_c)$ evidenced by a change in sign in $\partial\rho/\partial T$ as reported previously.[37,38] However, ρ reported herein is nearly an order of magnitude lower than those of the polycrystalline samples presumably due to the reduced grain-boundary effects since the CoO_2 layers in the planar grains are connected laterally in the epitaxial thin films. We also note that there is little anomaly in ρ at ~ 175 K, where the magnetic susceptibility shows an anomaly for the samples having fractional Li contents.[35]

In order to investigate the type of conduction, we plot $\log \rho/\rho_{300\text{ K}}$-$T^{-1}$ and $\log \rho/\rho_{300\text{ K}}$-$T^{-1/3}$ in Figs. 2(b) and 2(c), respectively, where $\rho_{300\text{ K}}$ is the resistivity at 300 K. The diverging behavior of ρ with $T \to 0$ of the $x=0.87$ sample is not as strong as that expected in an activated-type conduction, $\rho \propto \exp(\Delta/k_B T)$ [Δ is the energy gap in the density of states (DOS) about the chemical potential, μ], but is indicative of a variable-range-hopping (VRH) conduction, where $\rho \propto \exp(T_0/T)^{1/(d+1)}$ (d is the dimension of the hopping conduction[44]). One can see that the two-dimensional VRH conduction, $\rho \propto \exp(T_0/T)^{1/3}$ with $T_0 = 81$ K [dashed line in Fig. 2(c)] can reproduce the ρ-T curve of the $x=0.87$ sample fairly well at $T \lesssim 140$ K$(\equiv T^*)$, thus revealing a crossover in the conduction at T^*.[45] The low-T VRH conduction of the nonmetallic samples indicate that their DOS around μ is finite but the states therein are weakly localized [right column of Fig. 3(b) (Ref. 37)], most likely due to the disorder potentials originating from the random distribution of the Li ions. We do not exclude the possibility of a first-order Mott transition occurring upon increasing $x > 0.87$ (Refs. 38 and 46) so that an energy gap opens around μ at higher Li concentration due to correlation.

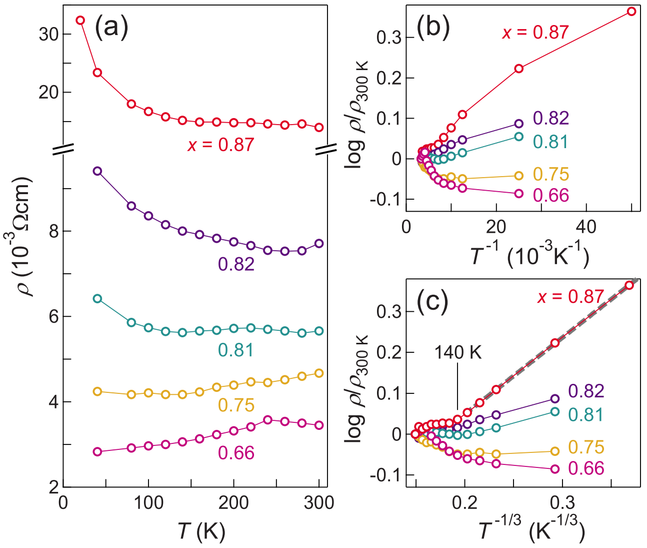

FIG. 2. (Color online) Temperature dependence of ρ of the Li_xCoO_2 epitaxial films. (a) A ρ-T plot. (b) A $\log \rho/\rho_{300\text{ K}}$-$T^{-1}$ plot for evaluating the activated-type conduction. (c) A $\log \rho/\rho_{300\text{ K}}$-$T^{-1/3}$ plot for evaluating the two-dimensional VRH. The dashed line indicates the linear relationship between $\log \rho/\rho_{300\text{ K}}$ and $T^{-1/3}$ at $T \lesssim 140$ K for the $x=0.87$ sample.

In contrast to Li_xCoO_2 at $x > x_c$ exhibiting a nonmetallic conduction, Na_xCoO_2 at high Na concentration exhibits a metallic conduction.[13] Since the distance between the A-ion layer and the CoO_2 sheet is shorter in Li_xCoO_2 than in Na_xCoO_2 (Li/Na ions in Li_xCoO_2/Na_xCoO_2 are located in an octahedral/prismatic oxygen environment[27]), the low-energy excitations occurring in the CoO_2 sheets of Li_xCoO_2 may be more strongly affected by the Li-ion disorder to show weak localizations at $x > x_c$, whereas those in Na_xCoO_2 may be less affected by the disorder so that they can propagate through as coherent quasiparticles[47,48] to show a metallic conduction [lower left of Fig. 3(b)]. The effect of disorder of the A-ion layers on the transport properties was also demonstrated in $Ca_{0.33}CoO_2$ thin films which can adopt two types of Ca-ion arrangements: a defect-rich orthorhombic type and a defect-poor hexagonal type showing nonmetallic and metallic conductions, respectively.[49]

Figure 3(a) shows S-T curves of the Li_xCoO_2 epitaxial films. The positive value of S in the whole temperature and composition range confirms that the carriers are holes in Li_xCoO_2. One can see that S is increased with increasing x and the S-T curve of the $x=0.87$ sample exhibits a peak of magnitude ~ 120 μV/K at ~ 140 K. Note that this temperature coincides with T^* determined from the ρ-T analysis. In the polycrystalline bulk samples, the 140 K anomaly in the S-T curves appears as a hump feature.[37,38] The increase in S

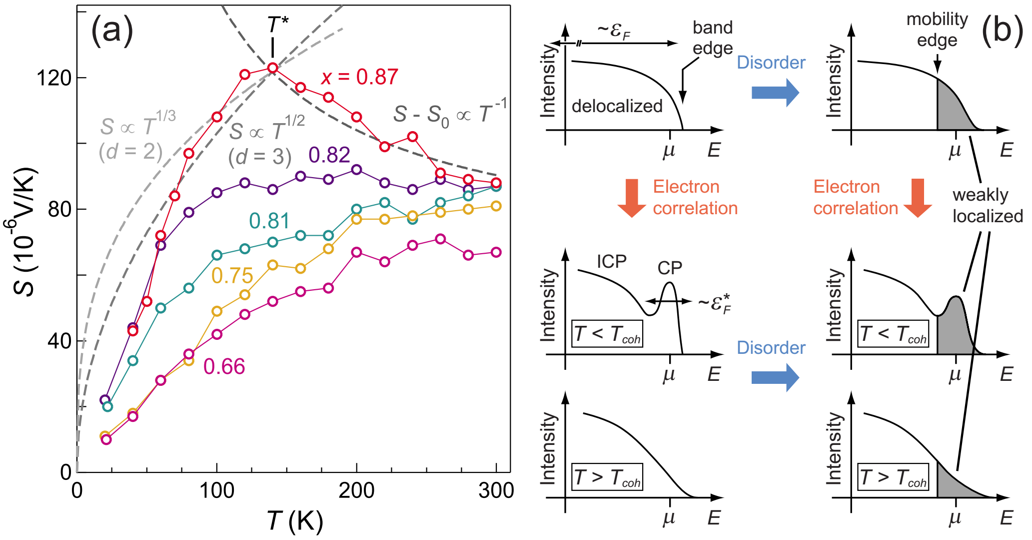

FIG. 3. (Color online) Temperature dependence of S. (a) S-T curves and theoretical curves for the VRH and the nearest-neighbor hopping (see text). (b) Excitation spectra near μ affected by disorder (right top), electron correlation (left bottom), and both disorder and correlation (right bottom). The spectrum of Na_xCoO_2 exhibits CP and incoherent part at $T < T_{coh}$ due to correlation (Refs. 47 and 48).

with x and the peak in the S-T curve at high Li concentration are similar to those observed in Na_xCoO_2 at high Na concentration,[13] and therefore, these features are considered to be common for A_xCoO_2 at high x. Such a peak in the S-T curves were also reported in the studies of carrier-doped transition-metal compounds[50] such as Cu_xTiSe_2,[51] $Fe_3O_{4-x}F_x$,[52] $(CaOH)_xCoO_2$,[53] and Fe_xZrSe_2.[54] On the other hand, the S-T curves for the $x \leq 0.75$ samples are almost linear in T up to ~ 100 K, indicating the metallic conduction consistent with $\partial\rho/\partial T > 0$.

The behavior of S approaching to 0 with decreasing T instead of diverging as $S \propto 1/T$ of an activated-type conduction[37] further supports that the DOS of the nonmetallic samples is finite around μ as shown in Fig. 3(b). When the conduction is a VRH and the DOS around μ is a slowly varying function of energy, $S \propto T^p$, where $p = \frac{d-1}{d+1} (<1)$,[50] so that the S-T curves exhibit negative curvatures in contrast to $S \propto T$ (corresponding to $p = 1$) of a metallic conduction. We overlay on the S-T curve of $x = 0.87$ in Fig. 3(a) the theoretical relationship of the VRH for $d = 2$ and 3,[55] and find that the negative curvature of the S-T curve at $T < T^*$ is qualitatively reproduced by the theory. Thus, the analyses of ρ-T and S-T consistently indicate that, at least at $T < T^*$, the transport is carried by the low-energy excitations which are weakly localized due to disorder.

Now we investigate the origin of the crossover in the transport at $T^* \sim 140$ K. If the DOS is independent of T (a rigid-band picture), T^* can be understood as the onset temperature of the conduction carried by the delocalized states beyond the mobility edge [upper right of Fig. 3(b) (Ref. 56)]. However, a peak in the S-T curve also occurs in a *metallic* Na_xCoO_2 at high x,[13] and if the origin is the same as that of Li_xCoO_2 at $x = 0.87$, the crossover temperature T^* should be explained other than the VRH scenario *within the rigid-band picture*, since this picture is only applicable to nonmetallic materials. In fact, there are signatures of nonrigid-band evolution of the electronic structures[57–60] and strong electron correlations[38,46,61] in Li_xCoO_2.

We recall evidence for a crossover in the low-energy electronic excitations with T in the layered cobaltates: in the angle-resolved photoemission spectra of Na_xCoO_2 (Refs. 47 and 48) and Bi-Pb-Co-O,[47] the quasiparticle peak disappears above $T_{coh} \sim 200$ K [left bottom of Fig. 3(b)], so that the Bloch-Boltzmann description of the transport becomes invalid at $T > T_{coh}$. This may result in the crossover seen in the transport properties, i.e., $T^* \sim T_{coh}$. In the case for Li_xCoO_2 at $x > x_c$, the low-energy excitations in the coherent part (CP) are further affected by the disorder to show weak localizations [right bottom of Fig. 3(b)], and hence the VRH conduction at $T < T^*$. The smallness of the renormalized Fermi energy $\varepsilon_F^* \sim 100$ meV due to strong correlations[62–65] may be the origin of T_{coh} as well as T^* occurring at ambient temperatures.[11] The peak at T^* in the S-T curve can occur when crossovering into a high-T incoherent conduction,[66] where the carriers are viewed as classical particles hopping among the Co sites. Alternatively, temperature dependence in the rate of quasiparticle scatterings with spin fluctuations that develops in a so-called pudding-mold band may explain the peak in the S-T curves,[10] and therefore, determination of the band structures of A_xCoO_2 at high x is necessary.

In summary, we investigated S and ρ of the Li_xCoO_2 epitaxial thin films which showed a two-phase coexistence at $0.75 \leq x \leq 0.87$ similar to that reported for bulk Li_xCoO_2. The resistivities were nearly an order of magnitude lower than those of the bulk polycrystals, presumably due to the reduction in the grain boundary effects in the epitaxial films. First, a metal-nonmetal transition occurred at $x \sim 0.8$ in the biphasic domain, similar to those reported for bulk Li_xCoO_2. The nonmetallic conduction at high Li concentration implies that the Li-ion layers not only act as a charge reservoir for the CoO_2 sheets but also act as a source of disorder that strongly influence the conduction. Therefore, manipulating the strength of disorder through, e.g., changing the distance between the A-ion layer and the CoO_2 sheet would be a key to achieve high TE performance in A_xCoO_2. Second, we showed that the conduction of the nonmetallic samples exhibited an anomaly at $T^* \sim 140$ K, where the ρ-T curve deviated from the temperature dependence of the VRH and S showed a drastic increase resulting into a peak in the S-T curve at high Li concentration. We attributed T^* to a crossover temperature from a low-T VRH conduction to a high-T incoherent conduction influenced by strong electron correlations.

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