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Rearrangement of sodium ordering and its effect on physical properties in the Na_xCoO_2 system

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We systematically study Raman spectroscopy of cleaved Na_xCoO_2 single crystals with $0.37 \leq x \leq 0.80$. The Raman shift of A_{1g} mode is found to be linearly dependent on Na content, while the Raman shift of E_{1g} mode has an abnormal shift to high frequency around $x=0.5$. The abnormal shift is ascribed to the occurrence of Na rearrangement in O1 structure. Temperature-dependent Raman spectrum for $x=0.56$ sample shows that Na rearrangement transition from O1 structure to H1 structure occurs around 240 K. Electronic transport and susceptibility for the sample with $x=0.56$ show a response to the Na rearrangement transition from O1 to H1 structure and that different Na ordering pattern causes distinct physical properties. These results give a direct evidence to prove Na ordering effect on physical properties of Co-O plane.

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I. INTRODUCTION

The layered cobaltate Na_xCoO_2 has attracted much interest in strong correlation research area due to its rich physics.[1–3] As we know, the electronic ground state is strongly dependent on the Na content in Na_xCoO_2 (Ref. 3), in which the valence of Co ion can be tuned by Na content. Moreover, the change in Na content can also affect the structure of Na^+ ion layer. Early electron-diffraction and neutron-diffraction measurements reveal a kaleidoscope of Na^+ ion patterns as a function of concentration.[4–7] A detailed phase diagram of Na^+ ion layer structure was given by Huang *et al.*[6] As shown in Fig. 1, there are four different types of structure for Na^+ ion layer with different Na content: H1, H2, H3, and O1. In the four types of structure, there are three types of Na^+ ion site: $Na(1)(2b(0,0,1/4))$, $Na(2)(2c(2/3,1/3,1/4))$, and $Na(2)'(6h(2x,x,1/4))$. The occupation probability of the above sites depends on both Na content and temperature.[6] It is expected that different Na^+ ion pattern corresponds to distinct physical properties. The relationship between structure of Na^+ ion layer and physical properties of Co-O plane is believed to be an important key of understanding this system[3,6] and becomes an issue in recent researches.[8–16]

Recently, single-crystal neutron-scattering study reveals the formation of ordered sodium vacancies for $x > 0.5$. Inside each vacancy, there exists a Na monomer or a Na trimer occupying Na(1) sites that sit atop Co atoms.[8] This multivacancy model and Na trimer geometry are also proved by single-crystal synchrotron x-ray diffraction and can be used to explain the observed superstructures of $x=0.84$ and 0.71 crystals very well.[11] A recent scanning tunneling microscopy study also found that an unexpected Na trimer ordering is found for $x \leq 0.5$ samples.[13] This interesting finding makes us renew our understanding of Na ordering pattern. More and more theoretical and experimental progresses of Na ordering[8,11,14–16] show that Na ordering plays an important role in understanding the rich physical properties of Co-O plane. However, direct experimental evidence of relationship between Na ordering and physical properties of Co-O plane is still limited.[9] Here, we report on a systematic Raman study in Na_xCoO_2. It is found that an abnormal sodium dependence of E_{1g} mode occurs around $x=0.5$. Temperature-dependent Raman study indicates that a possible Na rearrangement transition from H1 to O1 phase defined by Huang *et al.*[6] occurs at $x=0.56$. Electronic transport and susceptibility for the sample with $x=0.56$ show that this kind of Na rearrangement transition makes different physical properties in this system. These results give direct evidence for Na ordering effect on the physical properties of Co-O plane.

II. EXPERIMENT

High quality single crystals of Na_xCoO_2 were grown using the flux method ($x=0.7$) and floating zone technique (x

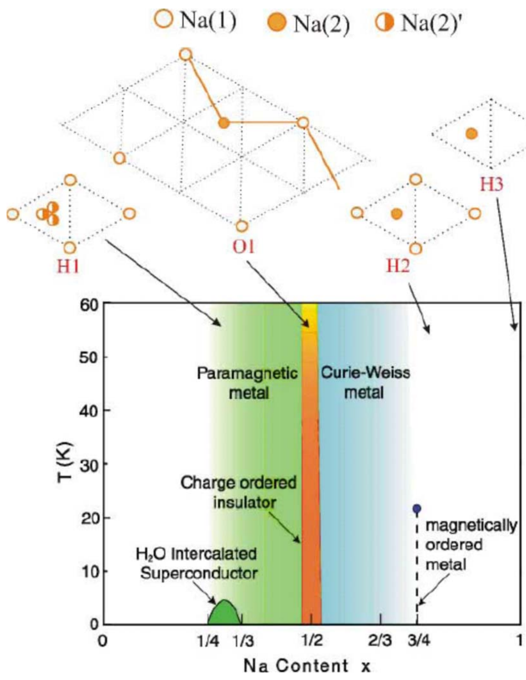

FIG. 1. (Color online) Correspondence between structure and properties in Na_xCoO_2 (figure Ref. 6). Upper panel: Schematic of the Na-ion distributions in the four Na_xCoO_2 phases. Lower panel: The electronic phase diagram.

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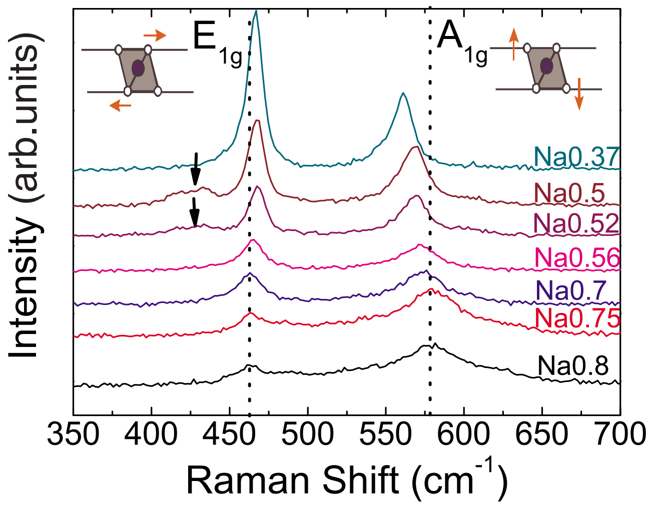

FIG. 2. (Color online) Raman spectra of Na_xCoO_2 single crystal from *ab* plane with $x=0.37$, 0.50, 0.52, 0.56, 0.70, 0.75, and 0.80 at room temperature.

$=0.75$ and 0.80). The Na_xCoO_2 sample with $x<0.7$ is prepared by sodium deintercalation of the $Na_{0.7}CoO_2$ singe crystals in solutions obtained by dissolving I_2 (0.2, 0.02, and 0.004 M) or Br_2 (6.0 M) in acetonitrile (M is "molar") for 4 days at room temperature. The x values of the samples were estimated by the same method as in previous paper.[17] Raman spectra were obtained on a LABRAM-HR confocal laser microRaman spectrometer using the 514.5 nm line from an argon-ion laser with in-plane light polarization. The single crystals were cleaved to obtain fresh surface before Raman measurements. The resistance was measured by an ac resistance bridge (LR-700, linear research). Magnetic-susceptibility measurements were performed with a superconducting quantum interference device magnetometer in a magnetic field of 7 T. It should be addressed that all results discussed as follow are well reproducible.

III. RESULT AND DISCUSSION

Figure 2 shows the Raman spectra for $x=0.37$, 0.50, 0.52, 0.56, 0.7, 0.75, and 0.80 at ambient temperature with the range from 350 to 700 cm^{-1}. Raman spectra of all samples are measured from *ab* plane with in-plane light polarization. In Fig. 2, all samples show two distinct Raman modes around 467 and 561 cm^{-1}, which can be attributed to Raman-active in-plane E_{1g} and out-of-plane A_{1g} vibrations of oxygen in CoO_6 octahedra, respectively.[18–23] The samples with $x=0.5$ and 0.52 show additional modes around 425 cm^{-1}, which is attributed to Na^+ ion ordering.[21] In addition, both of two samples show a charge ordering behavior at low temperature, which is consistent with the results by Foo *et al.*[3] and Wu *et al.*[17] These results indicate the sensitivity of this phonon to structural and electronic ordering processes. Two distinct systematic shifts are observed for A_{1g} and E_{1g} modes. With decreasing Na content, the A_{1g} mode shifts to low frequency and E_{1g} mode shifts to high frequency. The widths of A_{1g} and E_{1g} modes increase with sodium doping, and there exists a distinct broadening of A_{1g} and E_{1g} modes above $x\sim0.52$. This broadening of the two modes may come from instability of ordering structure of Na^+ ions. The systematic changes in related Raman shift of A_{1g} and E_{1g} with decreasing Na content are shown in Fig. 3. The Raman shift of A_{1g} mode is linearly suppressed with Na content. This result is consistent with previous data.[23,24] But it is surprising that the Raman shift of E_{1g} mode presents an abnormal shift around $x=0.5$, and this phenomenon is not observed in previous data.[24] Huang *et al.*[6] have proposed a structural phase diagram based on different structure of Na^+ ion layer. Present data indicate that the O1 structure may be corresponding to the abnormal shift of E_{1g} mode. Meanwhile, the above results also indicate that the E_{1g} mode is more sensitive to O1 structure than A_{1g} mode, which can be used as the fingerprint of O1 structure. It should be emphasized that the temperature dependence of Raman shift for E_{1g} mode also shows a T-linear behavior except for that observed in the samples of $x\sim0.5$ with Na ordering in O1 structure. Since the in-plane Na^+ ion ordering happens between two neighboring CoO_6 layers, it is also easy to understand why the out-of-plane A_{1g} mode has no distinct change. Recently, multivacancy model was proposed to understand the Na ordering phenomenon,[8] and Na rearrangement phenomena were also found for $x>0.5$.[7,10] The above results suggest that a possible Na rearrangement transition occurs around $x=0.5$ and E_{1g} mode is a good indicator.

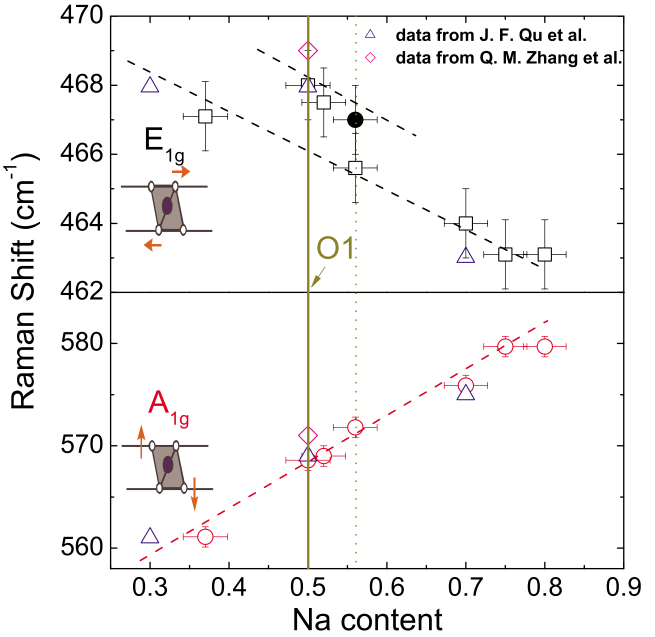

FIG. 3. (Color online) Na-content-dependent Raman shift of A_{1g} and E_{1g} modes at ambient temperature. Open squares stand for E_{1g} mode. Open circles stand for A_{1g} mode. Close circle stands for Raman shift of E_{1g} mode obtained by extrapolating the temperature-dependent Raman shift of E_{1g} mode below Na ordering transition temperature to room temperature for $x=0.56$ sample. Open triangle and diamond data come from Refs. 21 and 22, respectively. Dark yellow line stands for O1 ordering region phase defined by Huang *et al.* Dotted dark yellow line stands for Na reordering region defined in this paper. The black and red dash lines are guide for the eyes.

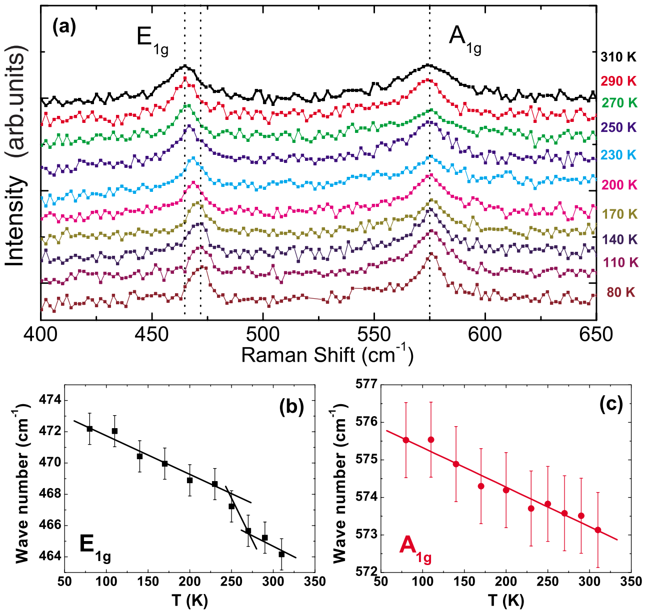

FIG. 4. (Color online) (a) Temperature-dependent Raman spectra of Na_xCoO_2 single crystal with $x=0.56$. Temperature-dependent Raman Shift of (b) E_{1g} mode and (c) A_{1g} mode for Na_xCoO_2 single crystal with $x=0.56$.

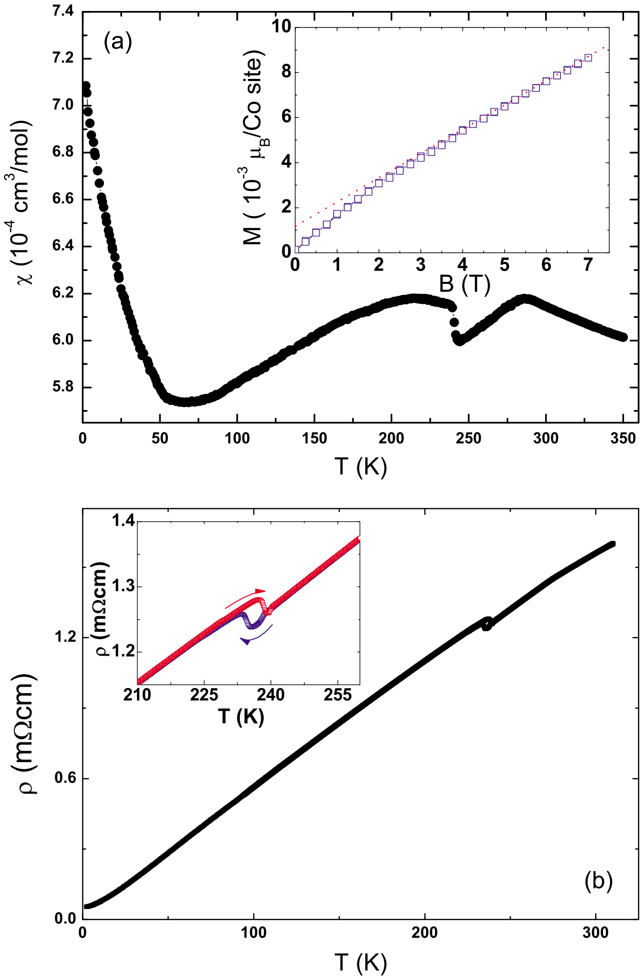

FIG. 5. (Color online) Temperature-dependent (a) susceptibility with $B=7$ T and $B \parallel$Co-O plane and (b) in-plane resistivity of Na_xCoO_2 single crystal with $x=0.56$. Inset in (a): Magnetization as a function of magnetic field up to 7 T at 4 K. Inset in (b): Temperature-dependent resistivity around structural transition temperature with cooling and heating measurement.

In order to further study the possible Na rearrangement transition, we chose $x=0.56$ sample and measured temperature-dependent Raman shift (80–310 K). In Fig. 4, temperature-dependent Raman spectrum for $x=0.56$ shows different temperature dependence for A_{1g} and E_{1g} modes. The temperature-dependent Raman shift of A_{1g} and E_{1g} modes is shown in Fig. 4(a). As shown in Figs. 4(b) and 4(c), A_{1g} mode linearly changes with decreasing temperature. Although a steplike change happens around $T_s \sim 240$ K, for the E_{1g} mode, Raman shift of the E_{1g} mode follows a T-linear dependence below and above T_s. According to the temperature dependence of Raman shift below T_s, a Raman shift could be obtained by extrapolating to room temperature. As shown in Fig. 3, the Raman shift of E_{1g} mode obtained by extrapolating to room temperature falls to the abnormal shift region around $x=0.5$ in Na ordering O1 structure. Since the sample is placed in an airtight box for low-temperature measurements, the signal-to-noise ratios of spectra are much lower than those in Fig. 2. We cannot see the weak Raman peak around 425 cm^{-1} below 240 K that exists in $x=0.5$ and 0.52 samples. Some previous data are also included in Fig. 3. It further indicates a Na ordering transition from O1 to H1 structure at $T_s \sim 240$ K with increasing temperature for the sample with $x=0.56$. Detailed information about this kind of Na ordering transition needs to be confirmed by further neutron- or electron-scattering experiment.

Temperature-dependent resistivity and susceptibility for $x=0.56$ are shown in Fig. 5 in whole temperature region ($2 \leq T \leq 300$ K). In Fig. 5(a), the susceptibility under $B=7$ T parallel to Co-O plane shows an anomaly around 240 K, being consistent with Na reordering transition observed in Raman study. Above 280 K, the temperature-dependent susceptibility shows a Curie-Weiss behavior. The data were fitted with the Curie-Weiss law $\chi = \chi_0 + \frac{C}{T+\theta}$. The fitting parameter θ is 124 K and the number of $S=1/2$ local spin is 0.14/Co site. This result is in agreement with the report for $x=0.7$ sample.[3] Below 240 K, the susceptibility shows a Pauli paramagnetismlike behavior. No antiferromagnetic ordering is observed down to 4 K unlike in $x=0.5$ sample.[3] A Curie tail exists below 50 K. The Curie tail is fitted with Curie-Weiss law, and the value of θ is 46 K and the number of $S=1/2$ local spin is 0.03/Co site. It indicates that the efficient number of $S=1/2$ local spin and antiferromagnetic correlation are reduced due to the Na reordering transition. A crossover from Curie-Weiss to Pauli paramagnetism is accompanied with Na reordering transition from H1 to O1 structure. A linear behavior is observed in field-dependent susceptibility at 4 K and only a tiny nonlinear behavior is observed below 2 T as shown in inset of Fig. 5(a). This also indicates that no ferromagnetic ordering happens. The ferromagnetic ordering shows up in $x=0.55$ and 0.52 samples.[17,25] In Fig. 5(b), the temperature-dependent resistivity shows a loop behavior around 240 K and the metal behavior is observed in the entire temperature region. Below 30 K, the

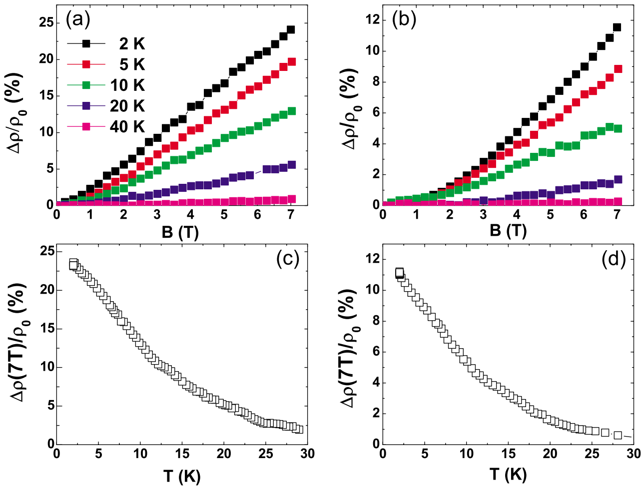

FIG. 6. (Color online) Magnetic-field-dependent in-plane magnetoresistance with external field (a) perpendicular to Co-O plane and (b) parallel to Co-O plane. (c) and (d) Magnetoresistance at 7 T as a function of temperature with external field (c) perpendicular to Co-O plane and (d) parallel to Co-O plane.

temperature-dependent resistivity obeys $T^{1.5}$ law. Between 30 and 200 K, a well-defined T-linear behavior is found. These characteristics are similar to that in Pauli paramagnetic metal for $x<0.5$, being consistent with the above magnetic properties. Isothermal magnetoresistance and temperature-dependent magnetoresistance under 7 T are shown in Fig. 6. A positive and monotonic magnetoresistance is observed as shown in Figs. 6(a) and 6(b). Below 30 K, a prominent positive magnetoresistance is observed under 7 T with a magnetic field both parallel and perpendicular to Co-O plane. This matched the $T^{1.5}$ behavior in resistivity. The maximum of magnetoresistance reaches 24% and 11% with B perpendicular and parallel to Co-O plane, respectively. These results indicate that strong magnetic fluctuation occurs below 30 K and a different paramagnetic state may exist at low temperature.

Recently, more and more experiments indicated that Na ordering is the key to understanding novel properties in Na_xCoO_2 system.[8,11,14–16] A plenty of Na ordering pattern and rearrangement transition between these different ordering patterns are found.[10,11] But direct evidence to prove the relationship between Na ordering pattern and physical properties of Co-O plane is still limited.[9] The above results give strong evidence that Na reordering transition from H1 to O1 structure can induce a crossover from Curie-Weiss to Pauli paramagnetic metal. Above Na reordering transition, a Curie-Weiss behavior similar to that observed in $x=0.7$ sample is confirmed by the temperature-dependent susceptibility. Below Na reordering transition, temperature-dependent resistivity and susceptibility are perfectly consistent with Pauli paramagnetic metal for $x<0.5$ sample. These results indicate a direct link between Na reordering transition and crossover from Curie-Weiss to Pauli paramagnetic metal. There exists contradiction about the abnormal "Curie-Weiss" metal for a long time. Recently, Shubnikov de Haas effect has been studied in $x=0.84$ and 0.71 samples.[12] They found that the Na ordering can reconstruct the Fermi-surface (FS) pockets and leads to the formation of local spin. In this picture, the crossover observed here can be attributed to another kind of reconstruction of FS pockets induced by Na reordering transition. Local spins are reduced and Pauli paramagnetism is enhanced by this kind of reconstruction of FS pockets. These results also shed light to the mechanism of charge ordering insulator for $x=0.5$ sample. The charge ordering insulator evolves from Pauli paramagnetic metal. Spin-density wave or charge-density wave mechanism is favor for this situation and early NMR result supports this picture.[26] But many recent experiments show that density wave mechanism cannot respond to insulator state for $x=0.5$ sample, and Na ordering effect is proposed to understand it.[27–29] The present data can be understood by density wave mechanism; but if there exists any other Na ordering pattern different from $x=0.56$ at low temperature similar to that in $x=0.5$, the density wave picture will be challenged.

IV. CONCLUSION

Raman spectroscopy of cleaved Na_xCoO_2 single crystals with $0.37 \le x \le 0.80$ was systematically studied. The Raman shift of A_{1g} mode is found to be linearly dependent on Na content, while the Raman shift of E_{1g} mode has an abnormal shift to high frequency around $x=0.5$. The abnormal shift is ascribed to Na^+ ordering in O1 structure. Na reordering transition from O1 to H1 structure around 240 K is proved by temperature-dependent Raman spectrum for $x=0.56$ sample. Electronic transport and susceptibility measurements for $x=0.56$ indicate that the Na ordering in different structures leads to distinct physical properties. Present results give a direct evidence for the relationship between Na ordering and physical properties of Co-O plane. The effect of Na ordering on physical properties is clearly presented.

ACKNOWLEDGMENTS

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