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Journal of Alloys and Compounds 262–263 (1997) 443–449

Journal of ALLOYS AND COMPOUNDS

Magnetism and electron transport phenomena of manganese oxide ion exchanger with tunnel structure

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Abstract

Conductivity, thermoelectric power (TEP) and magnetic susceptibility of the tunnel-type manganese oxides $K_{1.5}Mn_8O_{16}$ are reported. The conductivity and the TEP around room temperature suggest that the electrical conduction is governed by hopping of small-polarons. Three phase transitions are observed at T_1 (varies from 175 K to 215 K, batch-dependent), at T_2 (52 K) and at T_3 (20 K). The T_1 transition is considered to be a charge-ordering transition of Mn^{4+} and Mn^{3+} coupled with the ordering of the potassium ions in the tunnels. Weak ferromagnetism appears between T_2 and T_3 and disappears again below T_3. The anisotropic measurement of the susceptibility strongly suggests the occurrence of a helical magnetism below T_3. After the single crystals are soaked in conc. HNO_3 for a few days, a part of the potassium ions in the tunnels are removed. Besides, the activation energy is drastically reduced and the T_1 transition is suppressed. This suggests that the charge-ordering of Mn^{4+} and Mn^{3+} is very sensitive to the state of the tunnel cations. © 1997 Elsevier Science S.A.

Keywords: Manganese oxides; Mixed valence; Tunnel structure; Hopping conduction; Thermoelectric power; Weak ferromagnetism

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1. Introduction

Since manganese has a variety of oxidation states ranging from +II to +VII, solid compounds of manganese have a flexibility for charge transfer without a large destruction of the crystal structure. Therefore, they serve as a good solid state redox system. Among them, an interesting series is the multinary manganese oxides with porous structures as seen in zeolite. For example, hollandite-type $A_xMn_8O_{16}$ (A = K, Rb, or Pb, etc) includes one-dimensional tunnels within the MnO_6 octahedral framework [1]. Since the alkali cations etc. included in the tunnels have high mobility, they are easily replaced by other ions [2–5].

From a physical point of view, the redox property of the manganese oxides is often related to their high electrical conductivity. In addition, a manganese ion has a magnetic moment dependent on its valence ($S = 5/2$, 2, and 3/2 for Mn^{2+}, Mn^{3+} and Mn^{4+}, respectively). Therefore, it seems very attractive to investigate the effects of the chemical modifications (ion exchange, oxidation and reduction, etc.) on the physical properties (conductivity and magnetism, etc.). For that purpose, we have started a study of porous Mn oxides. So far, there have been only a few reports about the physical properties of $K_xMn_8O_{16}$ [6–8], and there is a discrepancy between the physical properties of the samples obtained by wet method and those by dry method. It is possible that the discrepancy is due

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PII S0925-8388(97)00351-4

to the difference in the state of the guest ions in the tunnels.

In what follows, we report the physical properties such as electric conductivity, thermoelectric power (TEP), and magnetic properties of $K_xMn_8O_{16}$ single crystals obtained by the hydrothermal method [6]. We also report the influence of cation exchange on the conductivity.

2. Experimental

Single crystals of hollandite-type $K_{1.5}Mn_8O_{16}$ were synthesized by the hydrothermal method using a test-tube autoclave [6]. Many needle-shaped single crystals were obtained. The typical size was $1 \times 0.005 \times 0.005$ mm^3. The crystals were characterized by X-ray powder diffraction and EPMA. From EPMA, only the atomic ratios K/Mn were obtained. No further chemical analyses were made. Electrical conductivities were measured by the dc four-terminal method. Gold wires were attached to a single crystal with carbon paste and the current was applied along the needle axis (the *c*-axis), which is parallel to the tunnels. TEPs of single crystals were measured by almost the same method as the second method in reference [9]. In the present experiments we used a chromel-constantan thermocouple. The temperature gradient was made along the *c*-axis. Magnetic measurements were done with a SQUID magnetometer (Quantum-Design MPMS-5) on a bundle of single crystals. Unfortunately, all the batches included some non-crystalline impurity in addition to needle-like $K_{1.5}Mn_8O_{16}$ crystals.

3. Results and discussion

For the measurements, we prepared three batches no. 1, no. 2, and no. 3. The results of EPMA show the K/Mn ratios are almost 1.5/8 for all the batches. As shown in Fig. 1, the hollandite structure has tunnels within the framework of MnO_6 octahedra. The potassium ions are located in the tunnels. If the tunnel sites were fully occupied by potassium ions, the composition should be $K_2Mn_8O_{16}$. Therefore, 1/4 of the sites in the tunnels are vacant in $K_{1.5}Mn_8O_{16}$. However, Strobel et al. pointed out that the crystals obtained by wet method can contain H_3O^+ and H_2O in the tunnels [7]. For simplicity, we ignore the possible H_3O^+ or H_2O guests and denote our samples as $K_{1.5}Mn_8O_{16}$.

As a consequence of the charge transfer from the potassium ions to the manganese ions, an Mn^{4+}/Mn^{3+} mixed-valence state is expected, giving rise to high electrical conductivity. In fact, the observed electrical conductivities at RT are as high as about 10 S cm^{-1}. The temperature dependence of the conductivities are shown in Fig. 2. All of the measured samples show almost activation-type behaviors. The activation energy, E_A/k_B obtained from the $\log \sigma$ vs. $1/T$ plot around RT, is about 1000 K regardless of the batch number. All the samples have a certain temperature below which the activation energy increases. We name this temperature T_1. The behaviors below T_1, and T_1 themselves, are strongly batch-dependent. The sample of batch no. 1 shows a sharp phase transition at T_1 (175 K) without thermal hysteresis, but that of batch no. 2 has a higher T_1 (215 K) and shows a thermal hysteresis around T_1. The sample of batch no. 3 does not show a clear phase transition at T_1, but shows a gradual increase in E_A below T_1 (about 210 K). The activation energies E_A/k_B far below the T_1 are 2600 K, 2200 K and 1700 K for no. 1, no. 2 and no. 3, respectively. We measured at least three samples of each batch and found that the sample dependence within the same batch is very small.

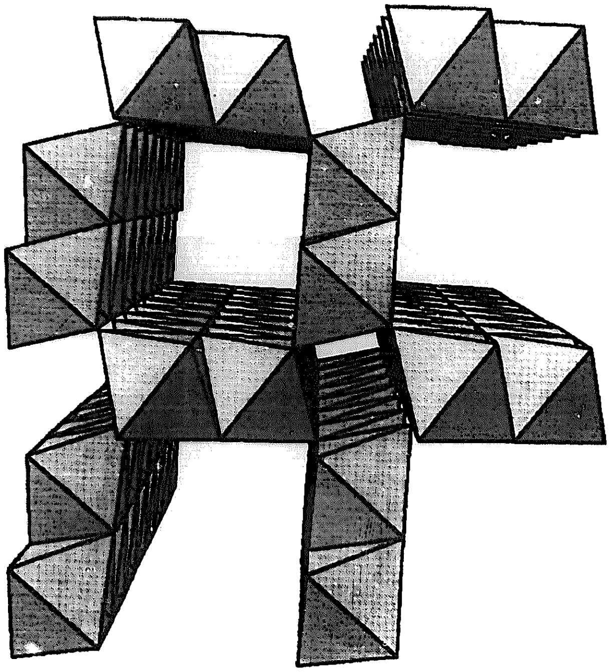

Fig. 1. Schematic crystal structure of $K_{1.5}Mn_8O_{16}$. The framework structure consists of edge-shared MnO_6 octahedrons. Potassium ions are included in the tunnels.

These activation behaviors in spite of the partial band filling suggest that the carriers are localized probably due to self-trapping by forming small-polarons. At least at RT, there is no evidence of static ordering of Mn^{4+} and Mn^{3+} sites from the X-ray analysis (N. Yamamoto, personal communication). Therefore, hopping rate of small polarons is large enough at RT. Based on a simple model of hopping conduction, the conductivity is given by,

$$\sigma = n(1-c)\tau_0^{-1}\frac{e^2l^2}{k_BT}\exp\left(-\frac{E_A}{k_BT}\right) \qquad (1)$$

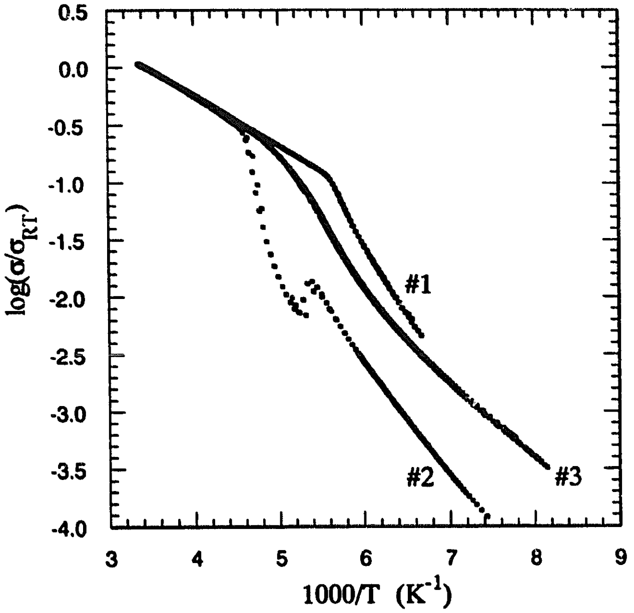

Fig. 2. Temperature dependence of the electric conductivities of $K_{1.5}Mn_8O_{16}$. The activation energy around RT is estimated at 1000 K from this plot.

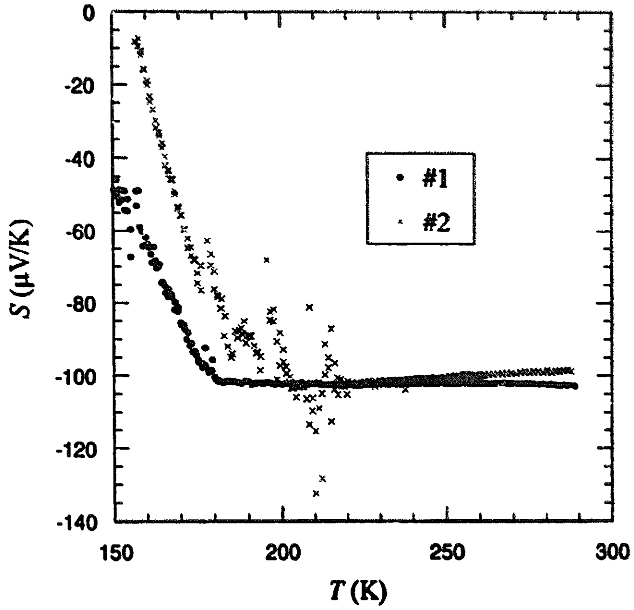

Fig. 3. Temperature dependence of the thermoelectric powers of $K_{1.5}Mn_8O_{16}$ (batch no. 1 and no. 2).

where n, c, τ_0^{-1}, l and E_A are the carrier density, the occupancy of the polarons, the trial rate of hopping, the hopping distance and the activation energy, respectively. Using a $\log(\sigma T)$ vs. $1/T$ plot, which is more appropriate for the estimation of E_A of the hopping conduction, E_A/k_B is estimated at about 1200 K. By putting the observed values, $\sigma = 10$ S cm^{-1}, $n = 5 \times 10^{21}$ cm^{-3}, $c = 1.5/8$, $l = 3$ Å and $E_A/k_B = 1200$ K, τ_0^{-1} is estimated at 1×10^{14} s^{-1}. Although this is slightly larger than the typical frequency of an optic phonon, the results are semi-quantitatively consistent with the small polaron model. There is a large difference between the data of our $K_{1.5}Mn_8O_{16}$ and that of $K_{1.33}Mn_8O_{16}$ reported by Strobel et al. [7]. The activation energy of $K_{1.33}Mn_8O_{16}$ around RT is almost four times larger than that of our samples. Furthermore, the T_1 transition is absent in $K_{1.33}Mn_8O_{16}$. It is notable that a superstructure due to the ordering of potassium ions is reported in $K_{1.33}Mn_8O_{16}$ [10]. This means that the Mn site energies are no longer equivalent and the polarons tend to be localized at the preferable sites. That is considered to be one of the reasons why $K_{1.33}Mn_8O_{16}$ has a larger activation energy.

In $K_{1.5}Mn_8O_{16}$, a part of Mn^{4+} is reduced into Mn^{3+} by the charge transfer from the included potassium atoms, which is expected to generate n-type carriers. As shown in Fig. 3, the TEP at RT is around -100 μV/K and almost independent of temperature down to T_1, below which the TEP begins to increase. The negative value is consistent with the expectation that the carriers are n-type. The temperature-independent behavior is explained by the hopping model of a highly correlated electron system. For the analysis of the TEP data, we assume that the on-site Coulomb energy for Mn e_g electron is infinite. In the present case, we can ignore the spin degeneracy of Mn because of strong Hund intraatomic exchange. Within these assumptions, the TEP is given by

$$S = -86.3\ln\left(\frac{1-\rho}{\rho}\right)\mu\text{V/K} \qquad (2)$$

using almost the same method as Chaikin [11], where ρ is the occupancy of the Mn sites by polarons. Putting the value 1.5/8 into ρ, the TEP is calculated at -127 μV/K independent of temperature. As well as the resistivity data, the TEP data are consistent with the small-polaron hopping picture.

Below T_1, both the activation energy of conductivity and the TEP increase with decreasing temperature. Equation (2) means that the increase in the TEP corresponds to the increase in the occupancy of polarons ρ. This may occur if the environment of Mn sites becomes no longer uniform, and the Mn sites with higher energy are excluded from the occupation by the polarons. Therefore, the results of the conductivity and the TEP strongly suggest that an ordering of Mn^{4+} and Mn^{3+} occurs below T_1. This conclusion reminds us of the 'Verwey' transition in Fe_3O_4. At present, the origin of the strong batch-dependence of the T_1 transition is not clarified but, as we explain later, it is possibly related to the inclusion of H_3O^+ or H_2O in the tunnels because our samples were prepared by wet method.

The magnetism of $K_{1.33}Mn_8O_{16}$ [7] and that of 'α-MnO_2' [6] have been already reported. The former shows an antiferromagnetic transition at $T_N = 18$ K

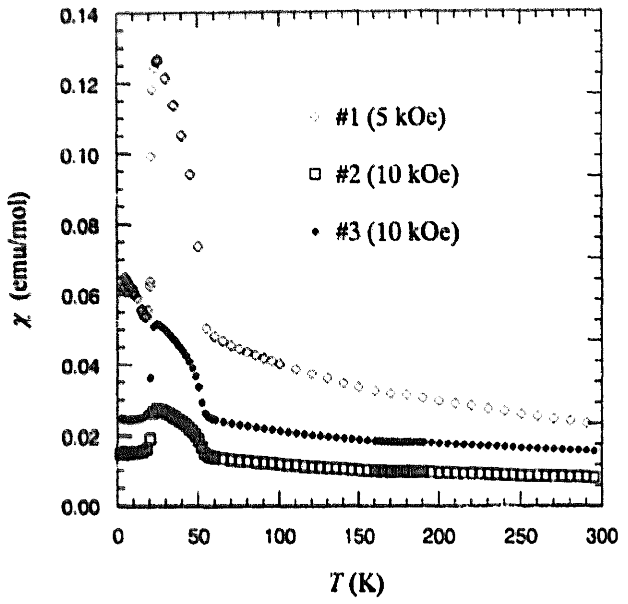

Fig. 4. Magnetic susceptibilities of $K_{1.5}Mn_8O_{16}$. They are batch-dependent because of the non-crystalline impurity.

and Curie-Weiss behavior above T_N, while the latter shows an antiferromagnetic transition at $T_N = 24.5$ K. Our magnetic susceptibility measurements on the present $K_{1.5}Mn_8O_{16}$ revealed the existence of two magnetic phase transitions at T_2 (52 K) and at T_3 (20 K). As shown in Fig. 4, the magnitude of the susceptibility is strongly batch-dependent because of the difference in the content of the non-crystalline impurity which we already explained. We can analyze the susceptibility above T_2 using the Curie-Weiss model except in the vicinity of T_1 where there is an anomaly. However, the estimation of the Curie constant C_{mol} and the Weiss temperature Θ is very sensitive to the content of the impurity as shown in Table 1.

Below T_2, the susceptibility steeply increases. In order to verify that this phase transition is not due to the impurity but due to $K_{1.5}Mn_8O_{16}$, we investigated the anisotropy. For that measurement, needle-like crystals were aligned in Apiezon-N grease. It was not successful in making a perfect alignment because there were so many single crystals (almost 10^4). Unambiguously, an anisotropy appears below T_2 as shown in Fig. 5. Between T_2 and T_3, the magnetization curve shows hysteresis due to a weak ferromagnetism as shown in Fig. 6. The direction of the spontaneous magnetization is perpendicular to the c-axis.

Below T_3, the weak ferromagnetism completely disappears and the susceptibility along the c-axis becomes larger than that along the direction perpendicular to the c-axis. Neither the T_2 nor the T_3 transition shows thermal hysteresis within the resolution of our instrument. Unlike collinear antiferromagnetism, a finite susceptibility seems to remain for all the directions at 0 K. This suggests that the low-temperature phase has a helical magnetic structure as has been discovered in β-MnO_2 [12,13]. Because there is a similarity in the crystal structure between β-MnO_2 and $K_{1.5}Mn_8O_{16}$, we can guess the magnetic structure of the latter making use of the data of exchange interaction of the former. The calculation of the magnetic structure by using a similar method to Yoshimori [12] suggests that $K_{1.5}Mn_8O_{16}$ also has a helical magnetic structure at 0 K (Sato et al., unpublished results). Below T_3, the $\chi(H\|c)$ shows larger susceptibility than $\chi(H\perp c)$ as shown in Fig. 5. This strongly suggests that the easy plane of spins is perpendicular to the c-axis as in β-MnO_2.

Table 1

Observed Curie constants C_{mol} (emu K/mol) and Weiss temperatures Θ (K). If the Mn ions are in the high-spin state, the C_{mol} should be 16.7 emu K/mol

	No. 1	No. 2	No. 3
200 K < T < 300 K	$C_{mol} = 9.38$	5.29	11.7
	$\Theta = -110$	−350	−450
60 K < T < 150 K	$C_{mol} = 10.3$	3.57	7.58
	$\Theta = -160$	−200	−250

The spontaneous magnetization between T_3 and T_2 is only about 0.3% of the calculated saturation magnetization of $K_{1.5}Mn_8O_{16}$. There are several possible explanations for the weak ferromagnetism. The first is the double exchange mechanism [14,15]. However, as we discussed before, the conduction electrons are considered to be almost localized below T_1. There-

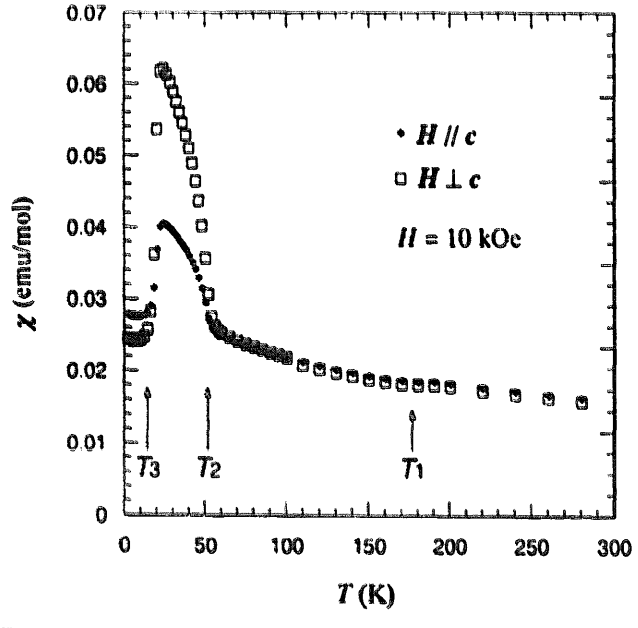

Fig. 5. Anisotropy in the magnetic susceptibility of $K_{1.5}Mn_8O_{16}$ (batch no. 3). The susceptibility becomes anisotropic below T_2. The appearance of the weak ferromagnetism (see the text) also in the $H\|c$ data is probably due to the imperfect alignment of the crystals.

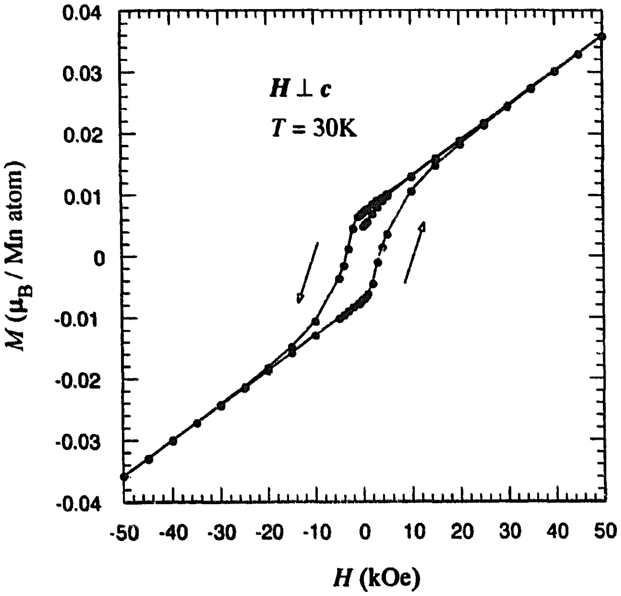

Fig. 6. Magnetization curve of $K_{1.5}Mn_8O_{16}$ (batch no. 3) at 30 K. The magnetic field was applied perpendicular to the c-axis. The weak ferromagnetism was observed only between T_2 and T_3.

fore, it is questionable that this mechanism is still effective below 50 K. The second possibility is the so-called Dzyaloshinsky–Moriya (D-M) mechanism [16,17]. In this mechanism, the antisymmetric exchange term $D(S_1 \times S_2)$ is added to the symmetric exchange term $JS_1\,S_2$. Because there is a mirror plane which bisects the nearest neighbor path, the D vector of the D-M interaction should be perpendicular to the c-axis. This conflicts with the fact that the spontaneous magnetization is perpendicular to the c-axis when the easy plane is perpendicular to the c-axis. In the above discussion, we ignored the effect of charge ordering of Mn^{3+} and Mn^{4+} which may occur below T_1. If we take it into account, D-M canting could be a possible mechanism. As another possibility, we propose a new mechanism of weak ferromagnetism as follows. In ordinary helical magnetic structures, no net magnetization appears because the magnetic moments cancel each other. However, in our case, there are two kind of spins, $S = 3/2$ for Mn^{4+} and $S = 2$ for Mn^{3+}. If the period of the helical magnetic structure λ_m has nothing to do with that of the charge ordering λ_c, a cancellation of magnetic moments occurs. On the other hand, if λ_c is an integral multiple of λ_m, complete cancellation does not always occur and weak magnetization can appear. From the composition of $K_{1.5}Mn_8O_{16}$, λ_c is expected to be eight times as large as the unit-cell parameter along the c-axis. Since the above concept can be regarded as a natural generalization of ferrimagnetism, we name the above mechanism 'helical ferrimagnetism'. In this model, we can explain that the observed spontaneous magnetization is very weak compared to that of an ordinary ferrimagnet and that it is perpendicular to the c-axis. The disappearance of the spontaneous magnetization below T_3 can also be explained by a change in λ_m due to the temperature dependence of the exchange interaction.

It is known that if the powder of $K_xMn_8O_{16}$ is soaked in conc. HNO_3, potassium ions are easily replaced by H_3O^+ [2–4]. In order to investigate the effect of the ion-exchange on the physical properties, we soaked single crystals of $K_{1.5}Mn_8O_{16}$ in conc. HNO_3 for a few days at RT. Although we have not pulverized the crystals, the EPMA analyses clearly show a decrease in the potassium content. This observation indicates that potassium ions have very high mobility especially in single crystals. The observed K/Mn ratio depends on the crystals, ranging from 0.06/8 to 0.10/8. Because we have not made the analysis of H_3O^+, it is not clear whether the reaction is only ion-exchange or accompanied by oxidization. Regardless of the batch number, the conductivities are drastically affected by the HNO_3 treatments as shown in Fig. 7. After the treatment, the activation energies around RT clearly decrease and the T_1 transitions are suppressed. This suggests that the charge-ordering transition at T_1 is coupled with the order-disorder transition of cations in the tunnels. The HNO_3 treatment suppresses the ordering of cations because a part of potassium ions are replaced by H_3O^+. As a result, the charge ordering of the Mn sites is also considered to be suppressed.

4. Summary

In order to know the conduction mechanism of the tunnel-type manganese oxides $K_{1.5}Mn_8O_{16}$, we measured conductivity and thermoelectric power (TEP). The activation-type behavior of the conductivity and temperature-independent behavior of the TEP suggest that the electric conduction is governed by a hopping of small-polarons. A phase transition observed at T_1 (varies from 175 K to 215 K, batch-dependent) is probably related to the charge-ordering of Mn^{4+} and Mn^{3+} induced by the ordering of the potassium ions located in the tunnels. The magnetic measurements revealed that there are two magnetic phase transitions at T_2 (52 K) and at T_3 (20 K). The magnetic susceptibility is paramagnetic above T_2. A weak ferromagnetism appears between T_2 and T_3. Below T_3, the spontaneous magnetization disappears again. Because finite susceptibility seems to remain at 0 K for all the field directions, helical magnetism is considered to appear below T_3. As a possible mechanism of the weak ferromagnetism, we propose 'helical ferrimagnetism' occurs when the period of the charge ordering is an integral multiple of that of the mag-

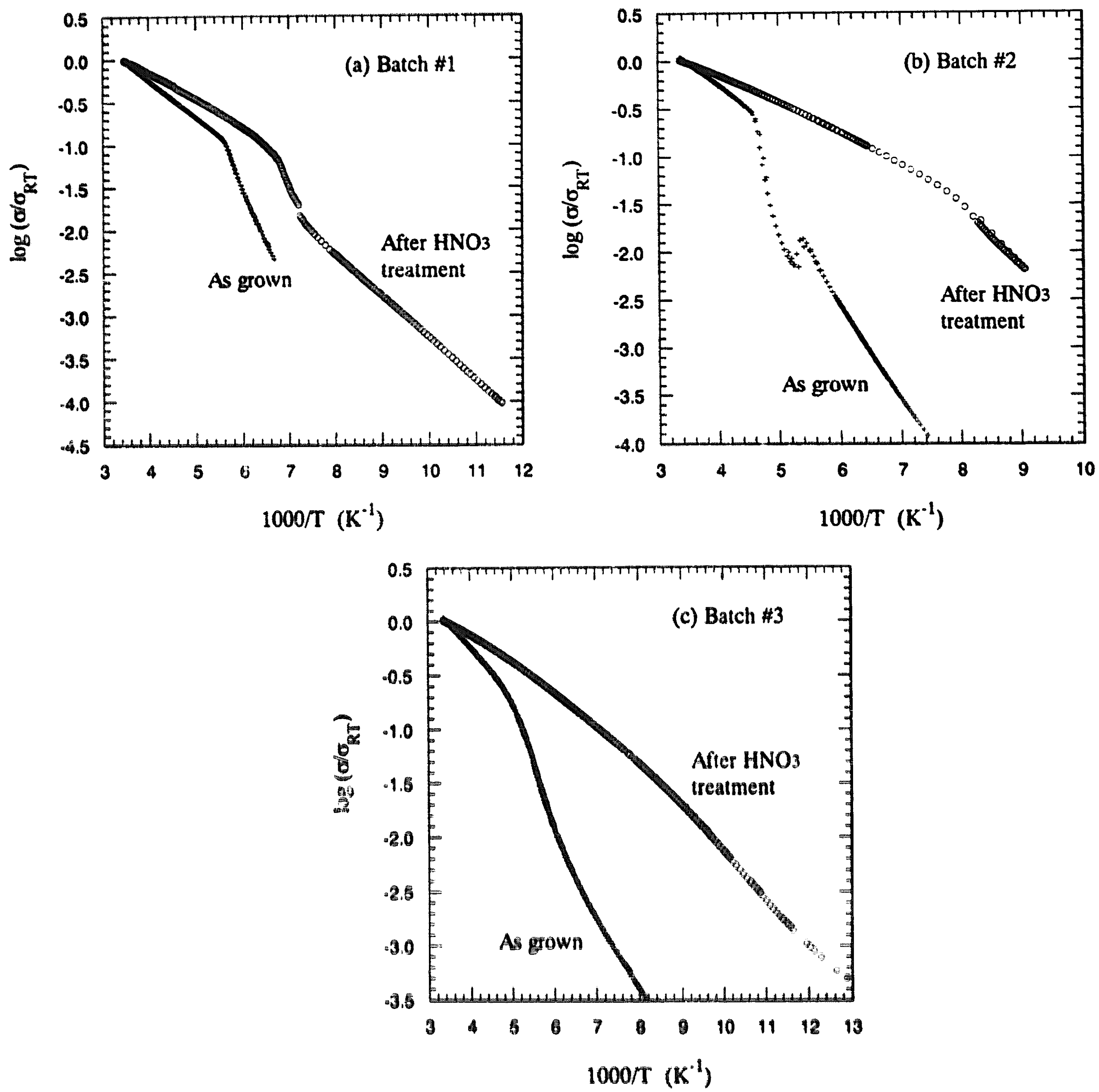

Fig. 7. The effect of the ion-exchange on the resistivity of (a) batch no. 1, (b) batch no. 2 and (c) batch no. 3. The $K_{1.5}Mn_8O_{16}$ crystals were soaked in conc. HNO_3 for a few days. The activation energies after the treatment are 670 K (no. 1), 610 K (no. 2) and 520 K (no. 3).

netic spiral. After the crystals are soaked in conc. HNO_3 for a few days, a part of the potassium ions in the tunnels are removed. After the soaking, the activation energy is drastically reduced and the T_1 transition is suppressed. This suggests that the hopping conduction and the charge-ordering of Mn^{4+} and Mn^{3+} are very sensitive to the state of tunnel cations.

Acknowledgements

The authors would like to thank R. Ohki for help in the EPMA analysis and Prof. S. Ramasesha for useful discussion.

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