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H Chen, T Wu, Y L Xie, R H Liu, G Wu, X F Wang and X H Chen[1]

Hefei National Laboratory for Physical Science at Microscale and Department of Physics,
University of Science and Technology of China, Hefei, Anhui 230026,
People's Republic of China

E-mail: chenxh@ustc.edu.cn

Abstract

We have measured susceptibility and angle-dependent magnetoresistance (AMR) on $K_{0.50}CoO_2$ single crystals. A possible magnetic structure similar to that of $Na_{0.5}CoO_2$, a G-type anti-ferromagnetic (AF) structure (both in-plane and inter-plane are AF), is proposed. At ~ 20 K, a loop is observed between zero-field-cooled (ZFC) and field-cooled (FC) susceptibility. The absolute value of magnetoresistance (MR) at 20 K is much larger than other cases with H applied within the ab plane. This could arise from the magnetic field being applied in the ab plane, leading to spin–flop of the small magnetic moment of $Co^{3.5-\delta}$ sites at 20 K to form in-plane ferromagnetic ordering, as observed in $Na_{0.52}CoO_2$.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The layered sodium cobaltate Na_xCoO_2 (NCO) has become a focus of research due to its peculiarly large thermoelectric power coexisting with low resistivity [1] and its unconventional superconductivity in $Na_{0.35}CoO_2 \cdot 1.3H_2O$ with $T_c \sim 5$ K. The phase diagram in this system is very rich and complicated [2, 3]. For $x < 0.5$, the material is a paramagnetic metal, while for $x > 0.5$ an unusual Curie–Weiss metallic phase is observed. At $x = 0.5$, its properties are more interesting; anti-ferromagnetic transition at $T_N = 87$ K and charge-ordering transition at $T_{CO} = 53$ K [3–5]. The magnetic structure of $Na_{0.5}CoO_2$ is very complicated. It shows magnetic frustration when it forms anti-ferromagnetic order below $T_N = 87$ because of a triangular lattice in CoO_2 layers. Neutron diffraction [5], NMR [4] and angle-dependent magnetoresistance (AMR) [6] studies indicate that two distinct Co sites exist with different magnetic moments in $Na_{0.5}CoO_2$ at low temperature; a stripe-like spin structure in the ab plane has been found in $Na_{0.5}CoO_2$. In this stripe structure, there are two kinds of chain formed by two different Co sites respectively: one is a $Co^{3.5+\delta}$–$Co^{3.5+\delta}$ chain and the other is a $Co^{3.5-\delta}$–$Co^{3.5-\delta}$ chain. These two chains are alternately arranged within the ab plane. The moment in the $Co^{3.5+\delta}$ site is larger than that

in the $Co^{3.5-\delta}$ site. The large moments form anti-ferromagnetic order below ~ 87 K with moments aligned within the ab plane [4, 6]. However, the small moments in the $Co^{3.5-\delta}$ site form anti-ferromagnetic order until ~ 20 K with moment along the c-axis [6]. The magnetic coupling of the small moment is very sensitive to the Na content. Our group has found that the magnetic coupling of small moments of $Co^{3.5-\delta}$ sites changes from anti-ferromagnetic for $x = 0.5$ to ferromagnetic for $x = 0.55$ [7]. Similar to Na_xCoO_2, other members of the family A_xCoO_2 (A = alkali metal) also display interesting and complex magnetic ordering. Recently, the K_xCoO_2 (KCO) system has been studied by a few groups. They found that K_xCoO_2 shares many similarities with Na_xCoO_2 [8, 9]. In $K_{0.5}CoO_2$, Watanabe et al observed two successive transitions with $T_N \sim 60$ K and $T_{CO} \sim 20$ K, which is about 30 K lower than those of $Na_{0.5}CoO_2$. The behavior of the two transitions in resistivity and susceptibility is the same as $Na_{0.5}CoO_2$ [9]. The transition T_N has been ascribed to in-plane anti-ferromagnetic ordering of the large moments of $Co^{3.5+\delta}$ sites, which has been proved by NMR and muon spin spectroscopy (μSR) [8, 9].

K_xCoO_2 with $x \sim 0.5$ shares many similarities to $Na_{0.5}CoO_2$, so that coupling of the small moments of $Co^{3.5-\delta}$ sites in K_xCoO_2 with $x \sim 0.5$ could be expected to be the same as $Na_{0.5}CoO_2$. To our knowledge, no one has studied the ordering of small moments of $Co^{3.5-\delta}$ sites

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[1] Author to whom any correspondence should be addressed.

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so far. In this paper, we studied the small moments $Co^{3.5-\delta}$ in $K_x CoO_2$ at $x = 0.5$ through angle-dependent magnetoresistance (AMR). Magnetoresistance (MR) provides insight into the coupling between charges and background magnetism. This is particularly valuable. As shown in our previous work, the small magnetic moments order is difficult to detect by magnetization measurements in the background of magnetic ordering with large magnetic moments [6].

2. Experimental procedure

The $K_{0.5}CoO_2$ single crystals were grown by the solution method using K_2CO_3–KCl flux. Starting materials K_2CO_3 and Co_3O_4 were mixed in the proportion K:Co = 1:2. The mixture was melted at $950\,°C$ for 20 h, then slowly cooled down to $750\,°C$ at a rate of $3\,°C\,h^{-1}$, and finally cooled to room temperature by furnace. The crystals were thin platelets and black in color. Typical dimensions of the crystals are $5 \times 5 \times 0.05\ mm^3$. Single crystals were characterized by x-ray diffraction (XRD) using Cu Kα radiations. As shown in figure 1, only (00*l*) diffraction peaks were observed and the lattice constant c was determined to be 1.245 nm, being consistent with that reported by Watanabe *et al* [9]. The actual chemical composition of the single crystals was determined by an inductively coupled plasma (ICP) atomic emission spectroscopy (AES) (ICP-AES) technique and x-ray energy dispersive spectrum (EDS). The obtained results from ICP-AES and EDS were found almost consistently to be K:Co:O = 0.50:1:2.

The electrical transport was measured using the alternating current (ac) four-probe method with an ac resistance bridge system (Linear Research, Inc.; LR-700P) in the temperature range 4.2–300 K. Magnetization was measured in the magnetic field $H = 500$ Oe using a superconducting quantum interference device (SQUID) magnetometer in the temperature range from 4.2 to 100 K. AMR was measured using a vibrating sample magnetometer from -6.5 to 6.5 T.

3. Experimental results and discussion

3.1. Resistivity and susceptibility

Figure 1 shows the temperature dependence of resistivity ($\rho(T)$) and magnetic susceptibility ($\chi(T)$) for single crystal $K_{0.50}CoO_2$. Two successive transitions can be seen at $T_N \sim 60$ K and $T_{CO} \sim 20$ K in both $\rho(T)$ and $\chi(T)$, respectively. These results are consistent with the report by Watanabe *et al* in $K_{0.5}CoO_2$. The inset of figure 1(a) shows the temperature-dependent resistivity in the temperature range from 4.2 to 300 K. It indicates that ρ increases sharply at $T_{CO} = 20$ K, suggesting the charge ordering; a hump shows up at around 13 K and the resistivity decreases slightly below 13 K. The differential curve $(d\rho(T)/dT)$ clearly shows the two successive transitions at $T_N = 60$ K and $T_{CO} = 20$ K, respectively. In figure 1(b), a significant suppression of χ is also observed at $T_N = 60$ K, indicating the onset

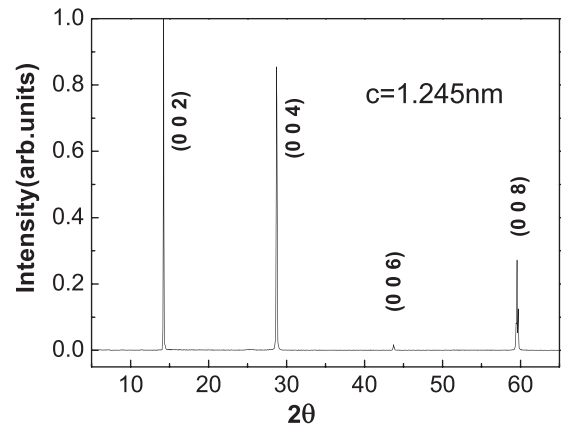**Figure 1.** Single crystal x-ray diffraction pattern of $K_{0.50}CoO_2$.

of anti-ferromagnetic ordering; a kink appears at 20 K. A small loop between ZFC and FC can be observed at around 20 K. It gives evidence that there exists a ferromagnetic-like behavior at around 20 K. As known in $Na_{0.5}CoO_2$, magnetic Bragg peaks appear below T_N and their intensity increases monotonically, no detectable change is observed at T_{CO} in neutron measurements [4, 5], which is also supported by ^{23}Na- and ^{59}Co-NMR experiments [4, 11]. Therefore, the magnetic order at T_{CO} cannot be detected by neutron measurements due to very small magnetic moment. It suggests that the magnetic structure change at $T_{CO} = 20$ K does not come from the large moment of $Co^{3.5+\delta}$ sites. Therefore, the magnetic ordering at $T_{CO} = 20$ K arises from the small moment of $Co^{3.5-\delta}$ sites. In other words, the ferromagnetic-like behavior comes from the small moment of $Co^{3.5-\delta}$ sites.

3.2. Magnetoresistance

In order to further investigate the origin of the loop around 20 K in susceptibility, we measured the resistivities ρ as a function of temperature at $H = 7$ T with $H \parallel$ Co–O plane and $H \perp$ Co–O plane. These results are shown in figures 2(a) and (b), respectively. It is found that the resistivity around 20 K is apparently reduced by the external magnetic field applied in the ab plane, while the effect of the magnetic field applied along the c-axis is ignored. It indicates that the in-plane magnetic field enhances the magnetic coupling, while the out-of-plane magnetic field almost has no effect on the magnetic ordering around 20 K. It suggests that the magnetic ordering comes from the magnetic moment of spin aligned with the ab plane, as observed in $Na_{0.55}CoO_2$ [7]. The isothermal MR with $\alpha = 0°$ ($H \parallel$ Co–O plane) and $\alpha = 90°$ ($H \perp$ Co–O plane) at 4, 17, 20, and 25 K is shown in figures 2(c) and (d), respectively. The α is the angle between magnetic field H and current I. It is found that a large negative MR is observed around $\sim$20 K both with $H \parallel ab$ plane and $H \perp ab$ plane. The MR with the $H \parallel ab$ plane and $H \perp ab$ plane changes from negative to positive with decreasing temperature. The negative MR maximum with $H \parallel ab$ plane and $H \perp ab$ plane MR is observed at 20 K, it gives evidence that the spin coupling of the magnetic moment is ferromagnetic
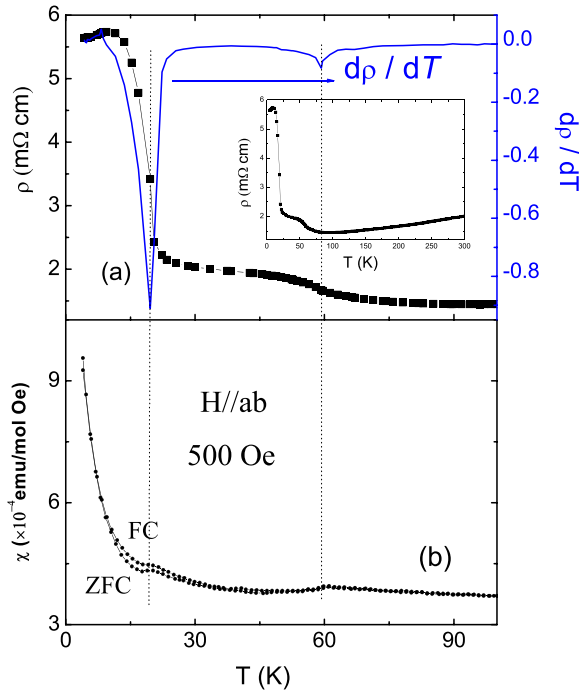
Figure 2. (a) Temperature dependence of electrical resistivity ρ in the temperature range from 4.2 to 100 K, the inset is the $\rho(T)$ in the entire temperature range. The derivative of resistivity as a function of temperature (b) magnetic susceptibilities χ as a function of temperature in zero-field-cooled and field-cooled processes under $H = 500$ Oe parallel to *ab* plane for a $K_{0.50}CoO_2$ single crystal.

under the magnetic field. Based on the study of the magnetic structure of $Na_{0.5}CoO_2$ and $Na_{0.55}CoO_2$ by Wang *et al*, the large magnetic moment of $Co^{3.5+\delta}$ sites cannot be changed by external magnetic field [6, 7]. Therefore, the large negative MR should come from the small magnetic moment of $Co^{3.5-\delta}$ sites. In other words, the effect of magnetic field around 20 K indicates that the coupling of the small magnetic moment of $Co^{3.5-\delta}$ sites is ferromagnetic at ~20 K. With decreasing temperature, a non-monotonic behavior appears at 17 K with $H \perp ab$ plane. A small, positive MR part monotonically appears below 2.5 T, then MR decreases to zero at 3.5 T and changes to negative MR with further increasing H. As discussed above, the negative MR is ascribed to ferromagnetic coupling between small moments. Therefore, the replacement of negative MR with positive MR below 3.5 T seems to be a reduction of ferromagnetic coupling between small moments. One possible explanation is that anti-ferromagnetic coupling becomes stronger than ferromagnetic coupling with decreasing temperature. It means that field induced ferromagnetic coupling is reduced by enhanced anti-ferromagnetic coupling. Meanwhile, no positive MR was observed with the $H \parallel ab$ plane. This suggests a stronger in-plane ferromagnetic coupling which is similar to $Na_{0.55}CoO_2$ [7]. With further decreasing temperature, the MR at 4 K with $H \parallel ab$ plane and $H \perp ab$ plane is positive. It suggests that the small magnetic moment of $Co^{3.5-\delta}$ sites in both the inter- and intra-plane couplings are anti-ferromagnetic and field induced ferromagnetic coupling is completely suppressed. The

isothermal MR shown in figures 2(c) and (d) is consistent with that observed in figures 2(a) and (b).

3.3. Angle-dependent magnetoresistance

In order to study the effect of spin ordering on the charge transport and to understand the behavior observed in figure 2, we investigated the angle-dependent in-plane MR behavior at different temperatures by rotating H in the plane consisting of the current and c axis, as shown in the schematic diagram. The magnetic field is fixed at 6.5 T during the measurement. As shown in figure 3, the AMR shows d-wave like behavior at 40 K. Such behavior is the same as that observed in $Na_{0.5}CoO_2$ [12]. At high temperature, only a large moment of the $Co^{3.5+\delta}$ site forms an anti-ferromagnetic order. Therefore, stripe-like spin ordering along $Co^{3.5+\delta}$–$Co^{3.5+\delta}$ exists in the Co–O plane. The d-wave-like behavior is believed to be a consequence of the rotation of the stripe direction with respect to the current direction. The MR is always negative at 20 K, and the maximum negative MR occurs at $\alpha = 0°$ and $180°$, that is the H lies within the Co–O plane. The two negative arms are the largest at 20 K and become small with further decreasing temperature, and eventually disappear at 4 K. The absolute value of MR at 20 K is about 16 times larger than at 10 K when H lies in the Co–O plane. It implies that spin–flop transition is induced by external magnetic field for the small moments of $Co^{3.5-\delta}$ sites at 20 K. The spin–flop transition makes the small moments of $Co^{3.5-\delta}$ sites form in-plane ferromagnetic coupling. In this sense, the loop observed between the ZFC and FC susceptibility in figure 2(b) can also be explained. The magnetic field induced spin–flop transition has also been observed in $Na_{0.52}CoO_2$ [12]. When $H \perp ab$ plane, the in-plane ferromagnetism is suppressed and the anti-ferromagnetism of small moments of $Co^{3.5-\delta}$ sites is enhanced [12]. Similar to the case of the Na–Co–O, in-plane anti-ferromagnetism is suppressed in $K_{0.50}CoO_2$ with $H \parallel ab$ plane, and the ferromagnetism of small moments of $Co^{3.5-\delta}$ sites is enhanced. With decreasing temperature, the positive arms become larger with $H \perp ab$ plane. This suggests that the coupling of the small moment of $Co^{3.5-\delta}$ sites in the inter-plane is anti-ferromagnetic. At 4 K only the positive arm can be seen. It seems to give evidence that the small moment of $Co^{3.5-\delta}$ sites forms G-type AF (both in-plane and intra-plane are anti-ferromagnetic).

Based on the above results, it is found that the large magnetic moment of $Co^{3.5+\delta}$ sites in $K_{0.50}CoO_2$ is the same as that in $Na_{0.5}CoO_2$ [13]. It forms in-plane anti-ferromagnetic ordering at $T_N \sim 60$ K. The inter-plane coupling of a small magnetic moment of $Co^{3.5-\delta}$ sites at 20 K is weaker. When the magnetic field lies in the ab plane, the spin–flop transition for the small magnetic moment of $Co^{3.5-\delta}$ sites is induced by an external magnetic field, forming in-plane ferromagnetic ordering as shown in figure 4(b). With decreasing temperature the inter-plane coupling of the small magnetic moment of $Co^{3.5-\delta}$ sites becomes stronger. Therefore, it is difficult to induce spin–flop transition by magnetic field, so that only positive arms can be observed at 4 K. It is proposed that the small moment of $Co^{3.5-\delta}$ sites forms G-type AF
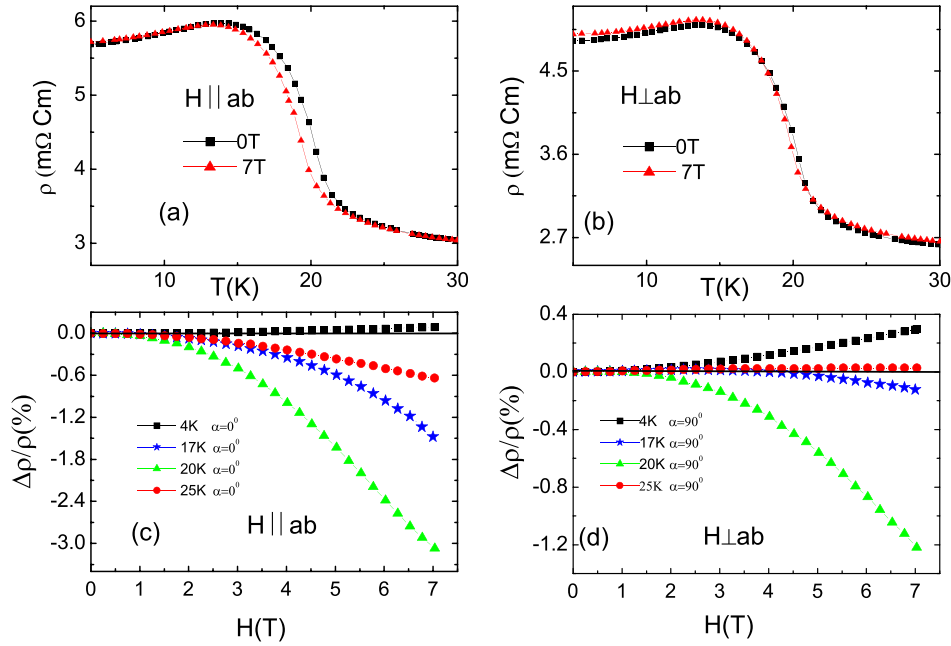
Figure 3. Temperature dependence of resistivity under different fields of 0 and 7 T with (a) $H \parallel$ Co–O plane and (b) $H \perp$ Co–O plane; isothermal magnetoresistance at 4, 18, 20 and 25 K with (c) $H \parallel$ Co–O plane and (d) $H \perp$ Co–O plane.
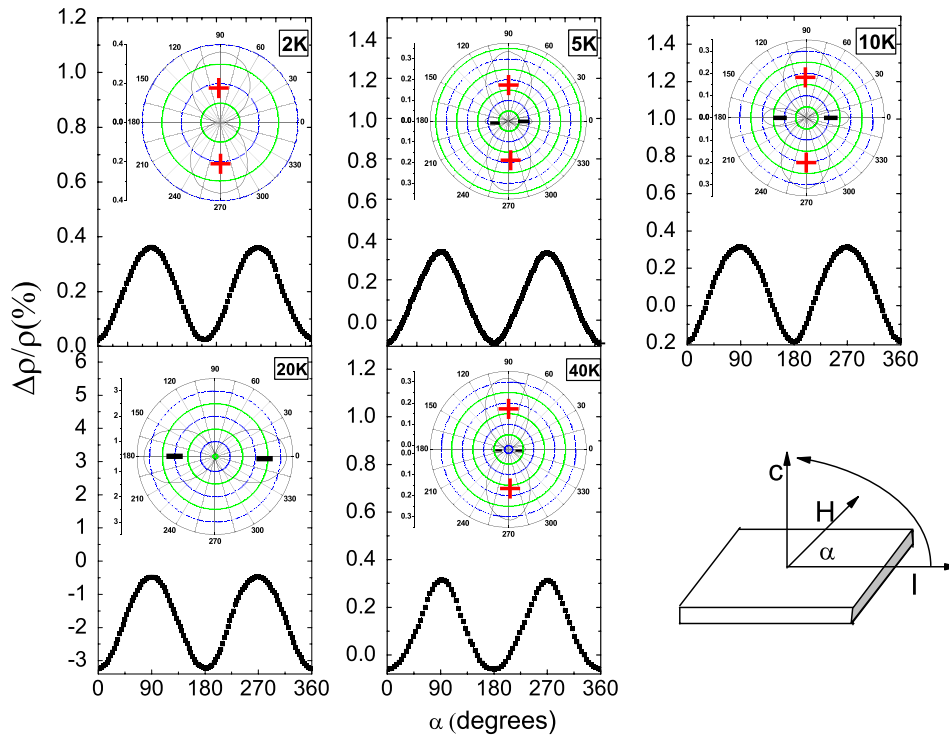

Figure 4. The angle dependence of isothermal MR and a polar plot for $K_{0.50}CoO_2$ under $H = 6.5$ T at different temperatures. The magnetic field H is kept in the plane consisting of the current and c axis when the sample is rotated, as shown in the schematic diagram.

(both in-plane and intra-plane are anti-ferromagnetic) as shown in figure 4(a). For $K_{0.50}CoO_2$, its magnetic structure at 4 K is the same as that of $Na_{0.5}CoO_2$ shown in figure 4(a). The transition around 20 K arises from spin ordering of the small magnetic moment of $Co^{3.5-\delta}$ sites. Magnetic field induced spin–flop transition around 20 K is analogous to that observed in $Na_{0.52}CoO_2$. However, similar magnetic field induced spin–flop transition cannot be observed in $Na_{0.5}CoO_2$ [12]. This difference may be explained by the difference between the distances of CoO_2 layers. It is well known that the inter-layer distance of $K_{0.50}CoO_2$ is larger than $Na_{0.5}CoO_2$, it makes the inter-plane coupling weaker than $Na_{0.5}CoO_2$.
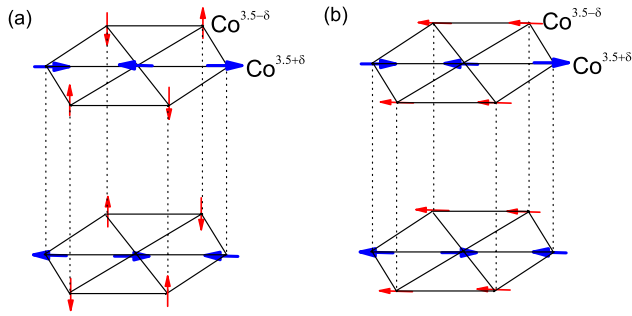
Figure 5. Magnetic structures for $Na_{0.5}CoO_2$ (a) and $Na_{0.52}CoO_2$ (b) proposed by Wang *et al* in [7, 10].

4. Conclusions

In this paper, we have measured susceptibility and angle-dependent magnetoresistance (AMR) on $K_{0.50}CoO_2$ single crystal and give a possible magnetic structure for it. Its magnetic structure is the same as that of $Na_{0.5}CoO_2$, which is G-type AF (both in-plane and intra-plane are AF). A loop is observed at ∼20 K between ZFC and FC susceptibility. Maximum MR is observed with H applied within the *ab* plane. Similar to the case of $Na_{0.5}CoO_2$, the small magnetic moments of $Co^{3.5-\delta}$ sites order anti-ferromagnetically around 20 K. A spin–flop for the small magnetic moment of $Co^{3.5-\delta}$ sites can be induced by an in-plane magnetic field to form in-plane ferromagnetic ordering.

Acknowledgments

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