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Large magnetothermal conductivity of $HoMnO_3$ single crystals and its relation to the magnetic-field-induced transitions of magnetic structure

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We study the low-temperature heat transport of $HoMnO_3$ single crystals to probe the magnetic structures and their transitions induced by magnetic field. It is found that the low-T thermal conductivity (κ) shows very strong magnetic-field dependence, with the strongest suppression of nearly 90% and the biggest increase of 20 times of κ compared to its zero-field value. In particular, some "dip"-like features show up in $\kappa(H)$ isotherms for field along both the *ab* plane and the c axis. These behaviors are found to shed light on the complex H-T phase diagram and the field-induced reorientations of Mn^{3+} and Ho^{3+} spin structures. The results also demonstrate a significant spin-phonon coupling in this multiferroic compound.

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I. INTRODUCTION

Magnetic-field-induced transition of magnetism is an outstanding phenomenon in the strongly correlated electron systems and is associated with many physical interests, such as the unconventional superconductivity,[1–3] the non-Fermi-liquid behaviors,[4] and the multiferroicity,[5] etc. It is known that multiferroicity is a result of strong coupling between magnetic and electric degrees of freedom in insulators and has received a lot of research interests because of its application usage. In this family of materials, for example, the rare-earth manganites $R\text{MnO}_3$ (R=rare-earth elements),[5–8] it is commonly found that the magnetic-field-induced transitions of magnetic structures are accompanied by the drastic changes in dielectric properties. Understanding the microscopic magnetic ordering across these transition boundaries is therefore very helpful for revealing the mechanism of magnetoelectric coupling, a topic of much current interest.

We select the hexagonal manganite $HoMnO_3$ as a representative object for studying the magnetic-field-induced transitions and their impacts on physical properties. This compound is ferroelectric below $T_c=875$ K and the moments of Mn^{3+} and Ho^{3+} ions display antiferromagnetic (AF) orderings at $T_{N,\text{Mn}}=75$ K and $T_{N,\text{Ho}}=4.6$ K, respectively. The peculiarity of $HoMnO_3$ is that it shows several transitions of the magnetic structure upon lowering temperature or increasing magnetic field, which results in a very rich H-T phase diagram at low temperatures.[8–12] Furthermore, these low-T field-induced transitions are confirmed to cause drastic changes in dielectric constant.[11] However, the low-T magnetic structures and the mechanisms of field-induced transitions are still not fully understood, in spite of a lot of experimental investigations using neutron scattering, optical and microwave techniques, etc.[13–17] This is due to the complexity of Mn^{3+} and Ho^{3+} magnetism in this compound. The Mn^{3+} ions form triangular planar sublattices and the AF exchange coupling among Mn^{3+} moments is geometrically frustrated. As a result, below $T_{N,\text{Mn}}$, the Mn^{3+} moments are ordered in a configuration that the neighboring moments are 120° rotated. However, the homometric configurations of the Mn^{3+} moments in the triangular lattice are difficult to distinguish from each other.[8–17] It was assumed that the Ho^{3+} moments are orientated along the c axis with an Ising-type anisotropy, and their spin structures are not simple because the Ho^{3+} ions present in two different crystallographic sites. The formed two Ho^{3+} sublattices can order separately in either parallel or antiparallel orientations.[8,15–17] For these complexities, even the zero-field spin structures at low temperatures have not been completely clarified, let alone those in the field-induced phases.

Heat-transport behavior has recently received a lot of interests in studying strongly correlated electron systems and low-dimensional spin systems.[18–20] It has been found that the low-T heat transport can probe not only the transport properties of many kinds of elementary excitations, such as phonons, magnons, spinons, and quasiparticles in superconductors but also the coupling between crystal lattice and spins.[21–23] In addition, the heat-transport behavior in magnetic field is an effective way to study the magnetic-field-induced quantum phase transitions,[24–28] for example, the field-induced AF ordering (which can be described as the magnon Bose-Einstein condensation) in spin-gapped quantum magnets.[29] In this paper, we show that the low-T heat transport of $HoMnO_3$ single crystals is very useful for probing the magnetic structures and the field-induced phase transitions. It is found that the spin-phonon coupling is extremely strong in this material and results in very strong field dependence of thermal conductivity (κ). In particular, the thermal conductivity is significantly suppressed at several critical fields, which are related to the transitions of magnetic structure. The suggestions provided by the present data on the magnetic structures of the low-T phases are discussed.

II. EXPERIMENTS

High-quality $HoMnO_3$ single crystals are grown by using a floating-zone technique. The crystals are carefully checked by using the x-ray Laue photograph and cut precisely along the crystallographic axes, with parallelepiped shape and typical size of $2.5\times0.6\times0.15$ mm^3. The thermal conductivities

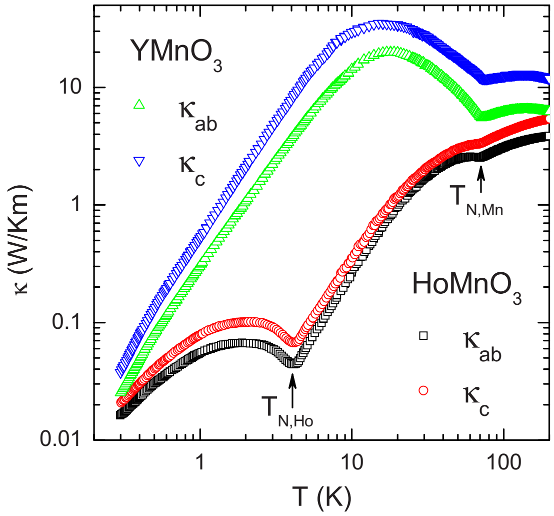

FIG. 1. (Color online) Temperature dependences of the *ab*-plane and the *c*-axis thermal conductivities of $HoMnO_3$ single crystals. The heat-transport data of $YMnO_3$ single crystals grown by the floating-zone method are also shown for comparison.

are measured along both the *ab* plane (κ_{ab}) and the *c* axis (κ_c) by using a conventional steady-state technique and two different processes: (i) using a "one heater, two thermometers" technique in a ^{3}He refrigerator and a 14 T magnet at temperature regime of 0.3–8 K; (ii) using a Chromel-Constantan thermocouple in a ^{4}He cryostat for zero-field data above 4 K.[29]

III. RESULTS AND DISCUSSION

Figure 1 shows the temperature dependences of κ_{ab} and κ_c of $HoMnO_3$ single crystals in zero field, together with those of $YMnO_3$ for comparison. These data essentially reproduce the results of a former report.[23] The heat-transport behavior of $YMnO_3$ is a typical one in insulating crystals,[30] except for a "dip"-like feature at ~70 K. The large phonon peaks at 15 K indicate a high quality of the crystals. The dip at 70 K is clearly related to the AF ordering of Mn^{3+} moments, where the spin fluctuations scatter phonons strongly. Similar feature at 70 K also appears in $HoMnO_3$. However, the heat transport of $HoMnO_3$ is very different from that of $YMnO_3$ in two aspects. First, the low-*T* phonon conductivity is much weaker in $HoMnO_3$, with the phonon peak completely being wiped out, suggesting very strong phonon scattering.[23] This is in good agreement with the evidences of spin-phonon coupling from other measurements.[17,31,32] Second, another diplike feature shows up at ~4 K, which corresponds to the AF ordering temperature of Ho^{3+} moments. It is important to notice that although Ho^{3+} moments are ordered below 4.6 K,[8] the strong phonon scattering seems to appear at temperature as high as 70 K. Such broad temperature regime for spin-phonon scattering is not likely to be caused only by the Ho^{3+} moments. It is already known that the Mn^{3+} sublattice has several spin reorientation transitions upon lowering temperature.[8–12] Obviously, these successive transitions strengthen the spin fluctuations in Mn^{3+} sublattice and contribute to the phonon scattering. In contrast, the reorientations of Mn^{3+} spin lattice do not occur in $YMnO_3$.

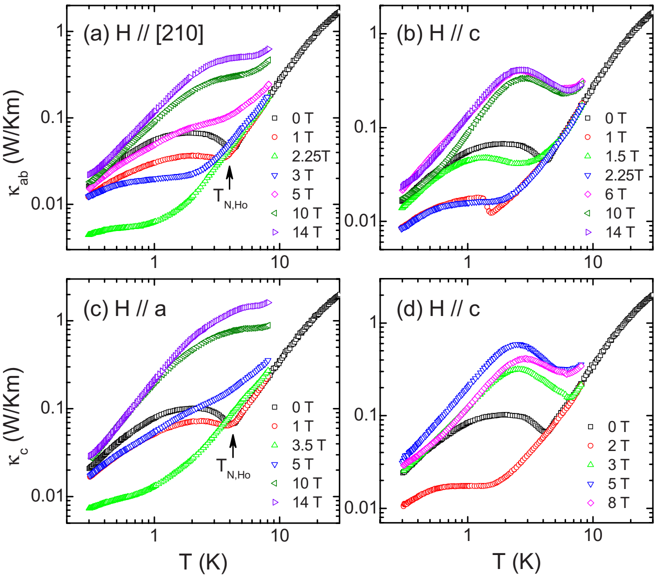

FIG. 2. (Color online) Temperature dependences of thermal conductivities of $HoMnO_3$ single crystals in both the zero field and several different magnetic fields up to 14 T. The heat current are applied along the *ab* plane or the *c* axis while the magnetic field applied either in the *ab* plane (along the *a* axis or [210] directions) or along the *c* axis.

The strong spin-phonon coupling suggests that the magnetic-field dependence of heat transport would be very useful for studying the low-*T* magnetic structures and their transitions. Figure 2 shows the temperature dependences of thermal conductivity in different magnetic fields up to 14 T, which clearly show an extremely large magnetothermal effect. By passing, it is worthy of pointing out that the magnetic field produces so strong torque, especially for $H \parallel c$, that the samples can be completely destroyed. This makes the measurement very difficult and it is almost impossible to get high-field data in some field directions. It can be seen in Fig. 2 that a low magnetic field strongly suppresses the phonon heat transport and makes the zero-field dip of $\kappa(T)$ at $T_{N,\mathrm{Ho}}$ to be shallower and broader and to shift to lower temperatures. In high magnetic field, the heat transport is significantly enhanced, particularly at temperature regime of 2–6 K, in which the spin-phonon scattering seems to be the strongest in zero field. This clearly demonstrates that the high magnetic field weakens the phonon scattering by spin fluctuations. However, one should note that although the field dependence becomes rather weak in high fields and below 1 K, the temperature dependence of κ in high fields is still much weaker than the T^3 law, suggesting the remaining of some microscopic scattering on phonons.

The detailed magnetic-field dependences of thermal conductivity $\kappa(H)$ are shown in Fig. 3. The extremely strong coupling between phonons and magnetic excitations leads to so strong field dependence of κ that the magnitude of thermal conductivity can be suppressed down to ~10% at some particular low fields and be enhanced up to 20 times at 14 T. To our knowledge, such a large magnetothermal effect has

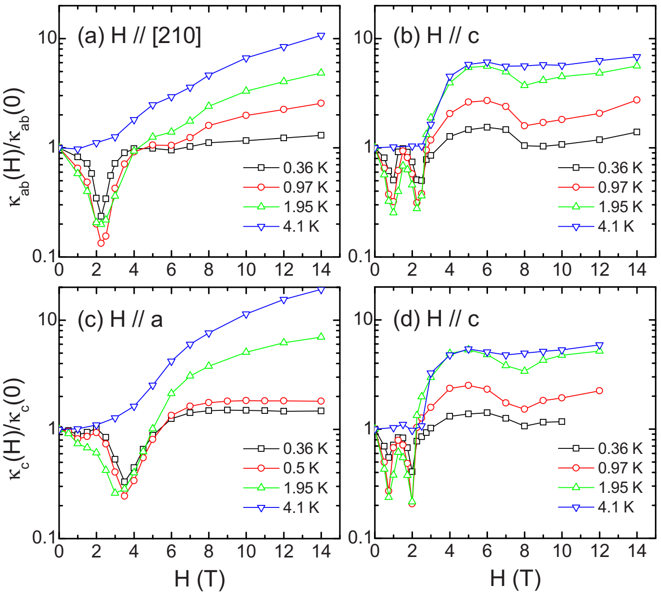

FIG. 3. (Color online) Magnetic-field dependences of thermal conductivities of $HoMnO_3$ single crystals at low temperatures.

not been observed in other materials including some rare-earth manganites.[33] At 4.1 K, where the zero-field $\kappa(T)$ data indicate the strongest spin-phonon scattering, the external magnetic field suppresses the magnetic excitations and reduces the phonon scattering. It is therefore easy to understand that both κ_{ab} and κ_c show significant enhancement with increasing field. Apparently, the thermal conductivity can be even larger before it gets saturated in very high magnetic field above 14 T ($\parallel ab$) and becomes at least comparable to that of $YMnO_3$, which is free from the spin-phonon scattering.

It is notable that the $\kappa(H)$ isotherms below 4 K are quite different from the higher-T results. An interesting phenomenon is that there is one dip in $\kappa(H)$ curves for magnetic field in the *ab* plane while there are two "dips" in $\kappa(H)$ for the magnetic field along the *c* axis. The characteristic of these dips is that the fields for the minimum κ are nearly independent of the temperature, which indicates an origin from the spin-flop transitions or spin reorientations.[34] In an AF ordered state, the Zeeman energy causes the magnon excitations to become gapless at the spin-flop field but the gap opens again at higher field;[21,34,35] consequently, the magnon scattering of phonons is the strongest at the spin-flop field, where the magnons are the most populated, and causes a diplike feature in the $\kappa(H)$ curve.

As we know, the low-T field-induced transitions for $H \parallel c$ have been intensively studied by the dielectric-constant, microwave, and neutron measurements.[10–12,15] The dip fields of $\kappa(H)$ at ~1 and 2 T are in rather good correspondence with the two successive transitions among the zero-field phase and some field-induced phases (named as "LT1" and "LT2" phases in Refs. 10 and 11). It should be pointed out that the low-T magnetic structure has actually not been completely understood. Between the two possibilities of the $P6_3cm$ and $P6_3c'm'$ space groups being the proposed zero-field Mn^{3+} magnetic structure,[8,9,13–16] more experiments supported the former one. Based on this, it was discussed that the magnetic-field-induced LT1 and LT2 phases are likely to have the magnetic structures of $P6_3c'm'$ and $P6_3cm$, respectively.[10] However, it has not yet been clarified how these two magnetic transitions are driven.

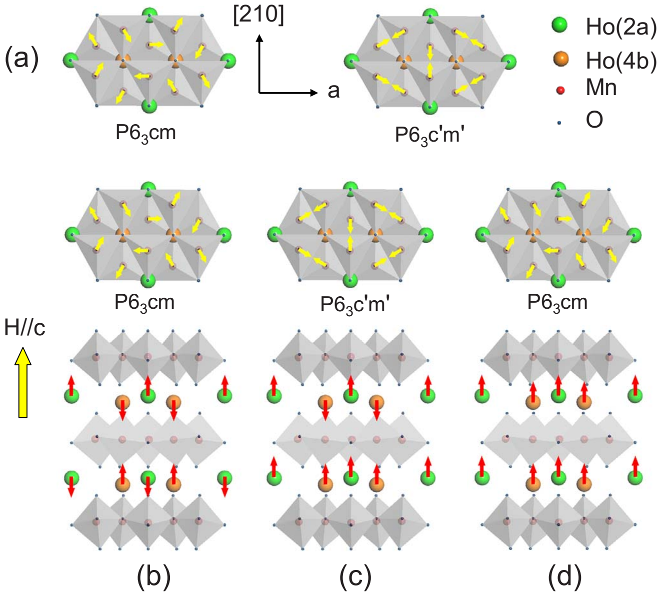

FIG. 4. (Color online) Magnetic structure of $HoMnO_3$ at low temperatures and those in applied magnetic field. Panel (a) shows the zero-field ($P6_3cm$) and high-field ($P6_3c'm'$) magnetic structures of Mn^{3+} moments for $H \parallel ab$. Panels (b)–(d) show the proposed two transitions of magnetic structure when the magnetic field ($H \parallel c$) is increasing. The two sublattices of AF Ho^{3+} moments are polarized separately at two critical fields. Correspondingly, the Mn^{3+} moments make 90° rotations twice.

Note that the *c*-axis field can hardly affect the magnetic structure of Mn^{3+} moments directly because they are strongly confined in the *ab* plane. It is the significant coupling between Mn^{3+} and Ho^{3+} moments that may lead to the change in Mn^{3+} sublattice when the Ho^{3+} moments change their directions or are polarized.[36] This possibility was first confirmed in a previous work, in which the polarization of Ho^{3+} moments formed by an external electric field causes a 90° rotation of Mn^{3+} sublattice.[8] It is known that the Ho^{3+} ions locate on two different positions of "2*a*" and "4*b*" (see Fig. 4) in the crystal lattice but the magnetism of Ho^{3+} ions is not very clear.[8,15–17] Some experiments suggested that the Ho^{3+} moments on 4*b* sites are antiferromagnetically ordered at low temperatures and those on 2*a* sites are disordered.[8,17] Apparently, the magnetic field along the *c* axis can induce only one sharp polarization transition of the 4*b* sublattice in this case. Therefore, the two diplike transitions observed in $\kappa(H)$ curves undoubtedly demonstrate that the zero-field Ho^{3+} magnetic structure must be different from that suggested configuration.[8,17] The present data point to a natural possibility as shown in Fig. 4(b), in which the Ho^{3+} moments on 2*a* and 4*b* sublattices are all antiferromagnetically ordered with opposite spin directions between two sublattices. This magnetic structure was previously proposed for an intermediate-temperature phase.[15] Correspondingly, the two-step sharp transitions of Ho^{3+} sublattice can cause the Mn^{3+} sublattice to perform 90° rotations twice, with the space group changing from $P6_3cm$ to $P6_3c'm'$ and then probably back to $P6_3cm$ (see Fig. 4), which is consistent with the suggestion in some earlier work.[10]

Since the low-T phase diagram for $H\|ab$ has not been explored,[12,37] the above direct comparison of heat-transport results with others is not available. In this regard, the present heat-transport data provide unprecedented information on the low-T phase diagram and phase transitions for $H\|ab$. It is clear that the thermal-conductivity data demonstrate a single spin-flop transition for $H\|ab$, which can only occur in the Mn^{3+} sublattice considering the Ising-type anisotropy of Ho^{3+} moments. Note that in Figs. 3(a) and 3(c), we show the data for magnetic field along two different in-plane directions, that is, [100] (along the a axis) and [210], as indicated in Fig. 4. It can be seen that there is a clear anisotropy of the transition field between these two directions. Similar phenomenon was observed in some other materials, for example, the parent compounds of electron-doped high-T_c cuprate $R_2CuO_4(R=Nd,Pr)$,[38,39] in which the critical fields for their noncollinear Cu^{2+} spin structure changing to a collinear one are dependent on the direction of magnetic field. It is not very difficult to obtain the theoretical explanation on such anisotropy of the spin-flop transition in the square spin lattice.[40] However, as far as the triangular spin lattice is concerned, it is still a remained question about how the spins rotate upon increasing field and how such rotation depends on the direction of the magnetic field.[41] Similar to the spin reorientations for $H\|c$, it is likely that the in-plane field may drive the zero-field magnetic structure of $P6_3cm$ symmetry undergoing a 90° rotation and changing to the $P6_3c'm'$ one at the critical field. By now, however, it is not possible to make a straightforward judgment on which direction is easier for the external field to drive the spin reorientation of the $P6_3cm$ spin structure. Nevertheless, the thermal-conductivity data indeed detect such anisotropy of transition field in an explicit way. Finally, the proposed magnetic structures and their transitions are summarized in Fig. 4.

IV. SUMMARY

The low-T heat transport of $HoMnO_3$ single crystals is found to be strongly dependent on the magnetic field, demonstrating an exceptionally strong spin-phonon coupling. Furthermore, the diplike transitions in low-T $\kappa(H)$ isotherms are found to be useful for clarifying the magnetic structures of the field-induced phases. The $\kappa(H)$ data for $H\|c$ suggest that Ho^{3+} moments form two AF sublattices and undergo two-step polarizations upon increasing field. Correspondingly, the Mn^{3+} sublattice undergoes two spin reorientations because of the strong interaction between Ho^{3+} and Mn^{3+} moments. The $\kappa(H)$ data for $H\|ab$ indicate a finding of spin-flop transition of Mn^{3+} sublattice, whose transition field shows an in-plane anisotropy.

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