Magnetic phase transitions and magnetoelectric coupling of $GdFeO_3$ single crystals probed by low-temperature heat transport

Z. Y. Zhao,[1] X. M. Wang,[1] C. Fan,[1] W. Tao,[1] X. G. Liu,[1] W. P. Ke,[1] F. B. Zhang,[2] X. Zhao,[3] and X. F. Sun[1,*]

[1]*Hefei National Laboratory for Physical Sciences at Microscale, University of Science and Technology of China, Hefei, Anhui 230026, People's Republic of China*

[2]*Department of Materials Science and Engineering, University of Science and Technology of China, Hefei, Anhui 230026, People's Republic of China*

[3]*School of Physical Sciences, University of Science and Technology of China, Hefei, Anhui 230026, People's Republic of China*

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The low-temperature thermal conductivity (κ) of $GdFeO_3$ single crystals is found to be strongly dependent on magnetic field. The low-field $\kappa(H)$ curves show two "dips" for $H \parallel a$ and only one dip for $H \parallel c$, with the characteristic fields having good correspondence with the spin-flop and the spin-polarization transitions. A remarkable phenomenon is that the sub-Kelvin thermal conductivity shows hysteretic behaviors on the history of applying the magnetic field; that is, the $\kappa(H)$ isotherms measured with increasing field are larger than those with decreasing field. Intriguingly, the broad region of magnetic field (~0–3 T) showing the irreversibility of heat transport coincides with that presenting the ferroelectricity. It is discussed that the irreversible $\kappa(H)$ behaviors are due to the phonon scattering by ferroelectric domain walls. This result shows an experimental feature that points to the capability of controlling the ferroelectric domain structures by magnetic field in multiferroic materials.

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I. INTRODUCTION

Low-temperature heat transport is an important physical property of solids and is useful for probing many kinds of elementary excitations, such as phonons, electrons, magnons, spinons, etc. Thermal conductivity (κ) is strongly dependent on the statistical laws of these excitations and their transport properties, which are directly related to the nature of the ground states of materials. For example, the temperature dependence of very-low-T thermal conductivity can directly show the purely phononic transport, the pairing symmetries of superconductors, the Fermi-liquid state of metals, and the nature of spin liquid in quantum magnets.[1–6] When the scattering between different types of quasiparticles is significant, the low-T heat transport can also be an effective way to detect such couplings; in particular, the spin-phonon or magnon-phonon couplings in insulating magnetic materials are sometimes easily revealed by the measurement of the magnetic-field dependence of thermal conductivity.[7–10] In cases of magnetic excitations either transporting heat or strongly scattering phonons, the magnetic phase transitions, including the changes of either the ground state or the spin structure, can be sensitively probed by the thermal conductivity measurements.[11–18] The purpose of this work is to get more information on the magnetic phase transitions and spin-phonon coupling of multiferroic materials by studying the low-T thermal conductivity.

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.[19,20] It is found that multiferroic materials usually present complex $H - T$ phase diagrams and multiple magnetic phase transitions, accompanied by the drastic changes of electric properties.[19–24] As a result, the low-T heat transport may show peculiar behaviors at these transitions. We choose $GdFeO_3$ as a candidate, which has a distorted perovskite structure with an orthorhombic unit cell ($Pbnm$).[25] It is known that Fe^{3+} spins form an antiferromagnetic (AF) order along the a axis below $T_N^{Fe} = 661$ K with a weak ferromagnetic (WFM) component along the c axis due to the spin canting in the ac plane,[26,27] which results from the Dzyaloshinskii-Moriya interaction.[28] The spin structure of Fe^{3+} ions can be expressed as $G_xA_yF_z$ in Bertaut's notation,[29] where G_x, A_y, and F_z stand for the spin components along the a, b, and c axes with the NaCl-type, the layered-type, and the ferromagnetic-type configurations, respectively. On the other hand, Gd^{3+} moments order antiferromagnetically along the a axis below $T_N^{Gd} = 2.5$ K and show a G_x-type spin structure.[24,29,30] The ferroelectric polarization appears below T_N^{Gd} and is considered to originate from the spin-exchange striction;[23,24,31] more exactly, the interaction between adjacent Fe^{3+} and Gd^{3+} layers with respective G-type AF ordering[29] drives Gd^{3+} ions to displace along the c axis so as to induce the ferroelectric polarization along the c axis. The magnetic-field dependencies of electric polarization (P) were carefully studied and believed to be related to the transitions of magnetic structures. In the case of $H \parallel a$, the simultaneous spin-flop transition of Gd^{3+} moments and reorientation of Fe^{3+} spins occur at ~0.5 T.[24,32] Across this transition, the magnetic structure changes from phase I ($G_xA_yF_z$ for Fe^{3+} spins and G_xA_y for Gd^{3+} moments) to phase II (Fe^{3+}, $F_xC_yG_z$; Gd^{3+}, G_z); thus, the electric polarization originating from the spin exchange striction shows a sudden drop. Upon increasing the magnetic field further, Gd^{3+} spins gradually turn to the direction of the magnetic field and they are completely polarized at ~2 T, where the magnetic structure changes from phase II to phase III (Fe^{3+}, $F_xC_yG_z$; Gd^{3+}, F_x). In the case of $H \parallel c$, the magnetic structure changes from phase I to phase IV (Fe^{3+}, $G_xA_yF_z$; Gd^{3+}, F_z) at ~2.5 T due to the simple spin-polarization transition of Gd^{3+} moments.[24] In both cases, the electric polarization decreases to zero as long as the Gd^{3+} moments are polarized at high field.[24]

In this work, we study the low-T thermal conductivity of $GdFeO_3$ single crystals and find that the magnetothermal conductivity is rather large, indicating a strong spin-phonon

coupling in this compound. The magnetic-field-induced spin-flop (or spin-reorientation) transition and spin-polarization transition are detected by $\kappa(H)$ isotherms. One peculiarity of the heat transport of $GdFeO_3$ is that it shows a hysteresis of the sub-Kelvin $\kappa(H)$ curves in a broad range of magnetic field. The possible origin of this irreversibility is discussed to be due to the ferroelectric-domain walls scattering on phonons. This result indicates the capability of magnetic field controlling the ferroelectric domain structures, which is a special but understandable phenomenon of multiferroic materials.

II. EXPERIMENTS

High-quality $GdFeO_3$ single crystals are grown by the floating-zone technique in a flow of oxygen.[24] The samples for thermal conductivity measurements are cut precisely along the crystallographic axes with typical dimension of $2.5 \times 0.6 \times 0.15$ mm^3 after being oriented by using the x-ray Laue photographs. The a-axis and c-axis thermal conductivities (κ_a and κ_c, respectively) are measured by 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.[10,15] In these measurements, the temperature gradient is 2%–5% and $\leqslant$2% of the sample temperature for temperatures below and above 30 K, respectively. The specific heat is measured by the relaxation method in the temperature range from 0.4 to 30 K using a commercial physical property measurement system (PPMS, Quantum Design).

III. RESULTS AND DISCUSSION

Before presenting the heat transport results of $GdFeO_3$ crystals, we show in Fig. 1 the low-T specific heat data. At very low temperatures, a large peak, which is apparently of magnetic origin, shows up. As can be seen from the inset to Fig. 1(a), this low-T peak seems to consist of a sharp peak at 2.2 K and a shoulderlike feature (or a weak peak) at ~1 K. Note that these data essentially reproduce those in an earlier report.[30] However, there is one small difference between two sets of data, that is, the data in Ref. 30 showed the sharp peak at 1.47 K and the shoulderlike feature at ~2 K. It was discussed that those two features are originated from the Néel transition of Gd^{3+} moments and a Schottky contribution, respectively. So the data in Fig. 1 indicate that the Néel temperature of Gd^{3+} moments of our $GdFeO_3$ crystal is 2.2 K, close to the value of a recent report by a susceptibility measurement.[24]

It can be seen that the magnetic contributions to the specific heat are important only at very low temperatures and are likely to be negligible above ~12 K, where the data in Fig. 1(a) shows a minimum. So one can make an estimation of phonon-specific heat from the high-T data in Fig. 1. It is known that in the temperature range $0.02 < T/\theta_D < 0.1$ (θ_D is the Debye temperature), one had better use the low-frequency expansion of the Debye function, $C = \beta T^3 + \beta_5 T^5 + \beta_7 T^7 + \cdots$, where β, β_5, and β_7 are temperature-independent coefficients.[33] It is found that this formula gives a precise fitting to the experimental data above 15 K, as shown in Fig. 1(b), with

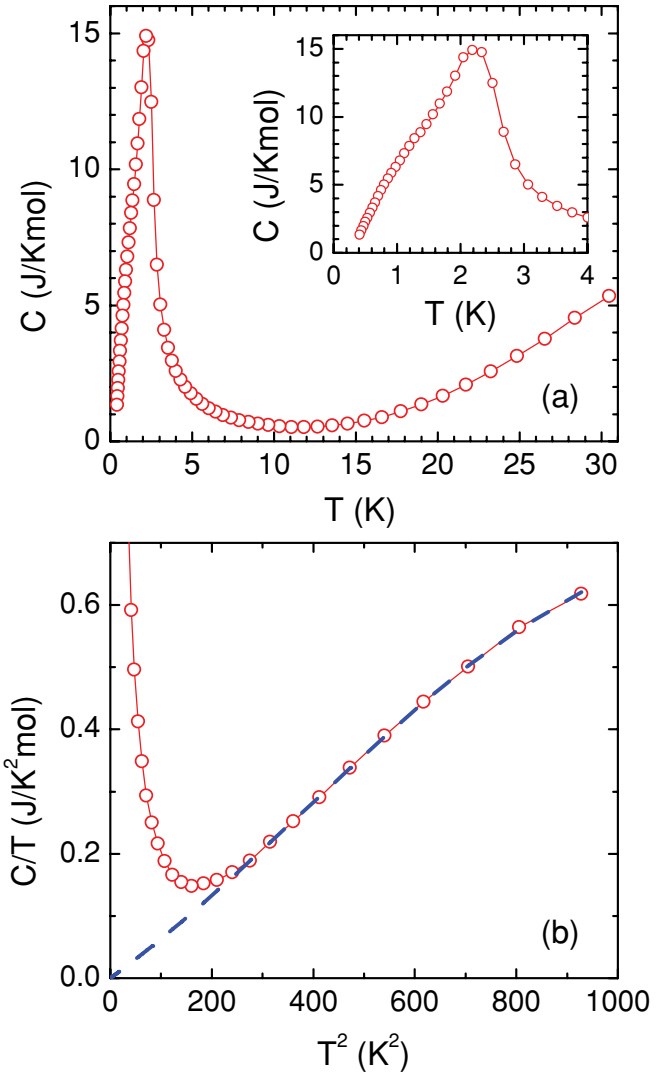

FIG. 1. (Color online) (a) Temperature dependence of the specific heat of $GdFeO_3$ single crystal below 30 K. The inset displays the data below 4 K, which show a sharp peak at 2.2 K and a shoulderlike feature at ~1 K. (b) The specific data plotted in C/T vs T^2. The dashed line shows the fitting to the high-T data by using the formula of phonon specific heat, that is, $C = \beta T^3 + \beta_5 T^5 + \beta_7 T^7$.

the fitting parameters $\beta = 5.90 \times 10^{-4}$ J/K^{4}mol, $\beta_5 = 4.52 \times 10^{-7}$ J/K^{6}mol, and $\beta_7 = -3.96 \times 10^{-10}$ J/K^{8}mol. Note that at very low temperatures, the T^5 and T^7 terms are negligible and the phonon specific heat shows a well-known T^3 dependence with the coefficient of β.

Figure 2 shows the temperature dependencies of κ_a for $GdFeO_3$ single crystals in zero and 14 T magnetic fields parallel to the a and c axes. As far as the zero-field data are concerned, they show a typical phonon transport behavior at relatively high temperatures.[1] In particular, the magnitude of the phonon peak at 18 K is as large as 250 W/Km, which is rather rare in the transition-metal oxides and indicates weak crystal defects or impurities. At low temperatures, however, there are some features showing a complexity of the phonon transport in this materials. First, even at very low temperatures the $\kappa_a(T)$ data show a distinct deviation from the T^3 law, a sign of the phonon boundary-scattering

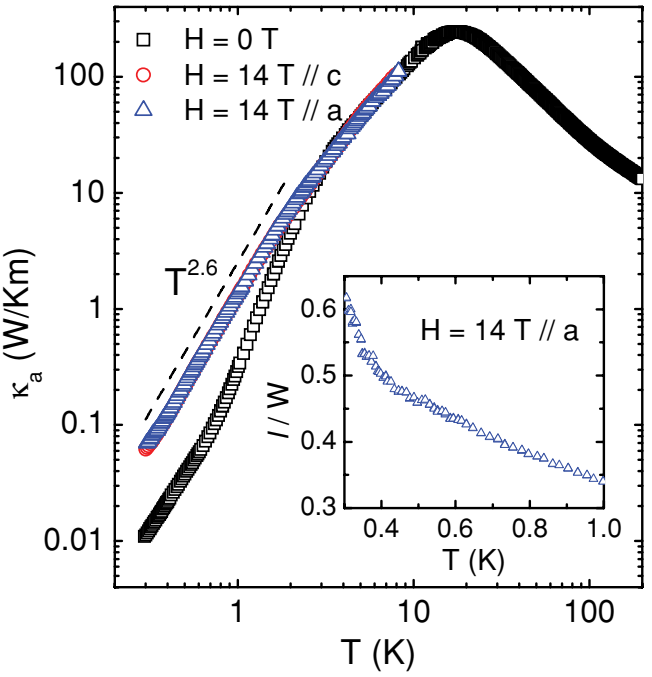

FIG. 2. (Color online) Temperature dependencies of the a-axis thermal conductivity of $GdFeO_3$ single crystal in zero and 14 T magnetic fields parallel to the a and c axes. The data in the 14 T field for two directions are nearly coincident. The dashed line indicates the $T^{2.6}$ dependence. The inset shows the temperature dependence of the phonon mean free path l divided by the averaged sample width W in the 14 T magnetic field.

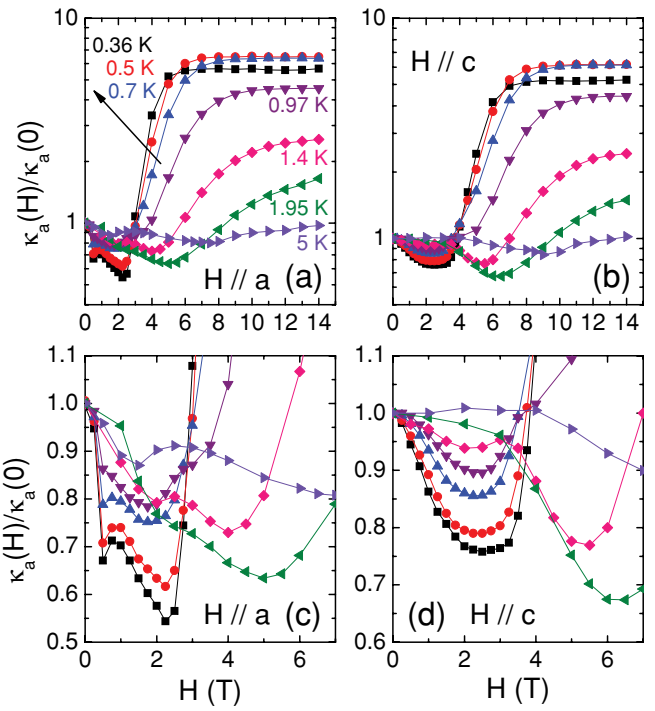

FIG. 3. (Color online) (a),(b) Magnetic-field dependencies of the a-axis thermal conductivity of $GdFeO_3$ single crystal. The magnetic fields are applied along the a or c axis. All the data are measured in the field sweeping-up process after zero-field cooling. (c),(d) Zoom in of the low-field data of panels (a) and (b).

limit, which apparently indicates the remaining of significant microscopic scattering of phonons.[1] Actually, the zero-field curve exhibits a weak kinklike temperature dependence below 2 K, which is likely due to the magnon-phonon scattering since the Gd^{3+} moments order antiferromagnetically below 2.2 K.[24,34] The effect of magnetic field on thermal conductivity seems to confirm this possibility. When a 14 T magnetic field is applied, the conductivities below 2 K become larger and the kink disappears, which clearly indicates the negative effect of magnons on the heat transport, considering that at low temperatures the magnons can hardly be thermally excited in high field. A $T^{2.6}$ dependence, which is very close to the boundary scattering limit, indicates that magnetic scattering on phonons is almost smeared out in the 14 T field. In addition, the effect of a strong magnetic field on κ_a is essentially isotropic for $H \parallel a$ and $H \parallel c$.

It is possible to estimate the mean free path of phonons at low temperatures and to judge whether the phonons are free from microscopic scattering at sub-Kelvin temperatures. The phononic thermal conductivity can be expressed by the kinetic formula $\kappa_{ph} = \frac{1}{3} C v_p l$,[1] where $C = \beta T^3$ is phonon specific heat at low temperatures, v_p is the average velocity, and l is the mean free path of phonon. Here $\beta = 5.90 \times 10^{-4}$ J/K^4 mol is obtained from the preceding specific-heat data and $v_p = 1930$ m/s can be estimated from Debye temperature Θ_D using the relations $\beta = \frac{12\pi^4}{5}\frac{Rs}{\Theta_D^3}$ and $\Theta_D = \frac{\hbar v_p}{k_B}(\frac{6\pi^2 Ns}{V})^{\frac{1}{3}}$,[33] where N is the number of molecules per mole and each molecule comprises s atoms, V is the volume of crystal, and R is the universal gas constant. So we can calculate l from the 14 T $\kappa(T)$ data and compare it with the averaged sample width $W = 2\sqrt{A/\pi} = 0.361$ mm,[1,35] where A is the area of cross section. As shown in the inset to Fig. 2, the ratio l/W increases with lowering temperature and becomes close to one at 0.3 K, which means that the boundary scattering limit is nearly established at such low temperatures. On the other hand, although not shown in the figure, the mean free path of phonons in the zero field is apparently several times smaller than that in the 14 T field, which obviously demonstrates the significance of microscopic phonon scattering in the zero field.

The magnon-phonon scattering is further evidenced by the magnetic-field dependencies of κ_a at low temperatures, as shown in Figs. 3(a) and 3(b). For both $H \parallel a$ and $H \parallel c$, the $\kappa_a(H)$ isotherms show a reduction at low fields followed by an enhancement at high fields. At sub-Kelvin temperatures, κ_a achieves a saturated value in high magnetic fields, but the magnitude weakens gradually with increasing temperature. Note that the high-field enhancement of thermal conductivity can be as high as ~700%, while the strongest suppression at low fields is ~50%, which clearly indicates that the coupling between magnons and phonons is pretty strong.[10] Another remarkable feature is that at sub-Kelvin temperatures there are two "dips" at low fields (<4 T) for $H \parallel a$, while only one shallow and broad dip emerges for $H \parallel c$. Moreover, the field-induced suppression of conductivity becomes weaker as increasing temperature. At higher temperatures above 1 K, another dip appears at high fields (>4 T) for both cases and it becomes broader and shifts to higher field with increasing temperature, which can be clearly seen in Figs. 3(c) and 3(d), suggesting its possible origin from phonon scattering by

paramagnetic moments.[1,7,8] We have also measured the c-axis thermal conductivity for both magnetic-field directions (see the Appendix) and found that the behavior of κ is essentially dependent on the direction of magnetic field rather than the direction of heat current, which again demonstrates the role of magnons in the heat transport in magnetic field.

Figures 3(c) and 3(d) show the details of low-field $\kappa_a(H)$ behaviors. As mentioned earlier, there are clear differences in the $\kappa_a(H)$ isotherms between $H \parallel a$ and $H \parallel c$. When the magnetic field is parallel to the a axis, the two dips of $\kappa_a(H)$ are at ~0.5 and ~2.25 T, which are weakly temperature dependent. Apparently, these two dips are directly related to the spin-flop transition and the spin polarization of Gd^{3+} magnetic structure,[17] as suggested by the low-T electric polarization data.[24] It was discussed that at 0.5 T the magnetic structure changes from phase I to phase II, which is associated with a simultaneous occurrence of the Fe^{3+} spin reorientation and the Gd^{3+} spin flop both from mainly along the a axis to mostly along the c axis. In Bertaut's notation, the magnetic structure changes from $G_xA_yF_z$ to $F_xC_yG_z$ for the Fe^{3+} spins and from G_xA_y to G_z for the Gd^{3+} moments. With further increasing the magnetic field, the Gd^{3+} moments gradually rotate to the direction of magnetic field and are fully polarized at ~2.25 T, where the magnetic structure changes to phase III (represented as $F_xC_yG_z$ for Fe^{3+} spins and F_x for Gd^{3+} moments). Since the magnon excitations become gapless at either the spin-flop field or the spin-polarization field, the quickly increased number of magnons can scatter phonons strongly and cause a drastic decrease of thermal conductivity,[10,17,18] manifested as those two weakly temperature-dependent dips in $\kappa(H)$ curves. When the magnetic field is applied along the c axis, there is no spin-flop transition of the magnetic structure; instead, the Gd^{3+} ions change their spin direction under a simple spin polarization process with increasing field.[24] It was discussed that the Gd^{3+} ion changes spin direction gradually from almost a axis to complete c axis at ~2.5 T, and the magnetic structure changes from phase I to phase IV ($G_xA_yF_z$ for Fe^{3+} spins and F_z for Gd^{3+} moments).[24] Consequently, there is only one broad dip in $\kappa_a(H)$ for $H \parallel c$.

Therefore, all the preceding results can be well understood in the scenario of phonon heat transport, with the significant scattering by magnetic excitations. However, this is not the whole story. It is found that the low-T thermal conductivity of $GdFeO_3$ is dependent on the history of applying the magnetic field.

As shown in Fig. 4, for both $H \parallel a$ and $H \parallel c$, the $\kappa_a(H)$ isotherms measured with increasing field are larger than those with decreasing field, forming a clear hysteresis at low temperatures. This phenomenon demonstrates that at very low temperatures, there is some peculiar channel of phonon scattering that is related not only to the magnetic field but also to the history of applying the field. As discussed on Figs. 2 and 3, the magnons are effective phonon scatterers in zero and low fields. However, they cannot simply produce an irreversible behavior of $\kappa(H)$ in such a broad field range from almost zero to ~3 T. In particular, the spin polarization is a naturally continuous transition and the hysteretic behavior cannot be expected across this transition. On the other hand, other microscopic phonon scatterers like point defects or dislocations in crystal structure are also irrelevant for two reasons.[1] First, the

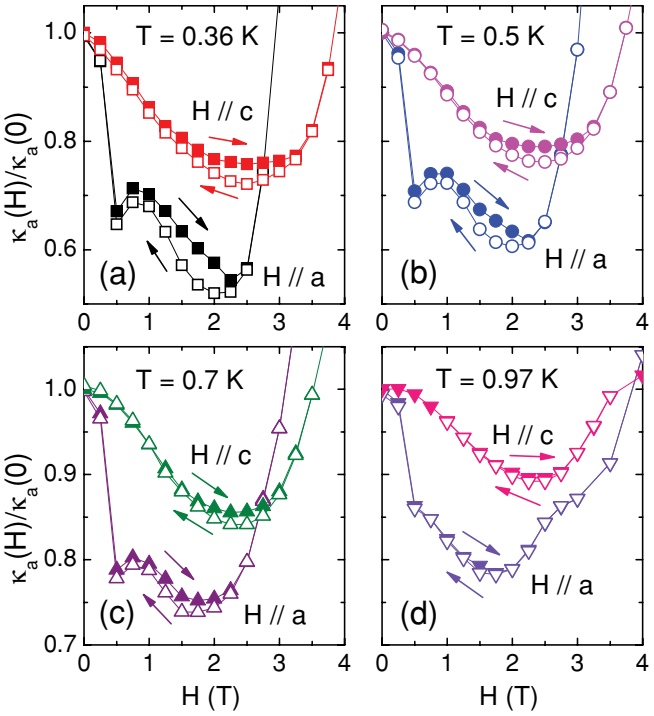

FIG. 4. (Color online) Low-field $\kappa_a(H)$ isotherms of $GdFeO_3$ single crystal at sub-Kelvin temperatures with magnetic field along the a and c axes. The data shown with solid symbols are measured in the ascending field after the sample is cooled in the zero field, while the open symbols show the data with the descending field, as indicated by arrows.

scattering processes from crystal imperfections have nothing to do with the external magnetic field, let alone the history of applying the field; second, these scatterings are known to be less effective upon lowering temperature, but the hysteresis becomes more pronounced with decreasing temperature.

Then, what else can be the origin of this kind of scattering that produces the hysteresis? Considering the development of hysteresis upon lowering temperature, a natural origin is related to the magnetic or ferroelectric domains in this multiferroic material, in which the domain walls can play an important role in scattering phonons at very low temperatures when the mean free path of phonons is long enough to be comparable to the interval of domain walls. It is known from the former work that the weak-ferromagnetism-related domains in $GdFeO_3$ can be produced only at very low field (<0.1 T).[24] Therefore, the ferroelectric domain walls are likely the main source of phonon scattering that is responsible for the $\kappa(H)$ irreversibility in the broad field range well above 0.1 T. In this regard, there are several experimental results supporting the origin of $\kappa(H)$ hysteresis from the ferroelectric domains. First, the electric polarization vs magnetic field $P(H)$ also showed the irreversible behaviors in the absence of electric field for both $H \parallel a$ and $H \parallel c$.[24] Second, the field range in which the hysteretic behavior of $\kappa(H)$ appears is almost the same as that exhibiting the hysteretic $P(H)$ curves.[24] Third, the relative magnitude of polarization for increasing field and decreasing field indicated that there are less ferroelectric domains when the field is increasing.[24] It is therefore in good agreement with the present observation

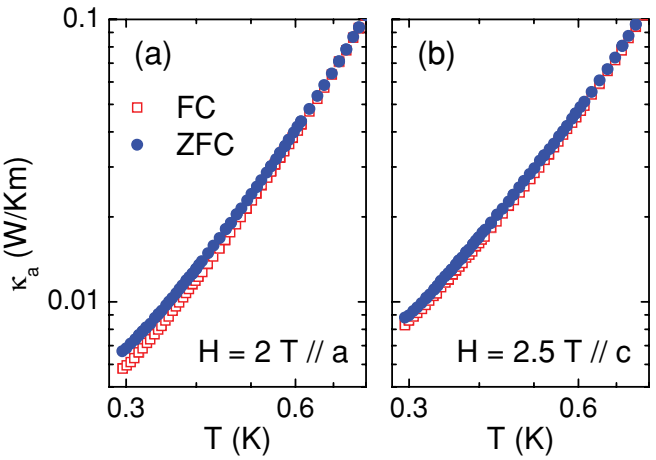

FIG. 5. (Color online) Temperature dependencies of the a-axis thermal conductivity of $GdFeO_3$ single crystal in a 2 T magnetic field along the a axis (a) and in a 2.5 T field along the c axis (b). The data are taken with slowly warming up the sample from the lowest temperature after field cooling or zero-field cooling.

that the thermal conductivity is larger in the increasing-field branch, which can be due to the weaker phonon scattering by domain walls. Furthermore, with increasing temperature the size of hysteresis diminishes and disappears completely above ~1 K, also in good agreement with the fact that the phonon scattering by boundaries is unimportant at high temperatures where the mean free path of phonons becomes much shorter than the averaged distance of domain walls.

The magnetic-field-induced irreversibility of κ can also be manifested in the $\kappa(T)$ curves, as shown in Fig. 5, measured in some characteristic fields by warming up the sample after zero-field cooling or field cooling to the lowest temperature. It is found that below 1 K the zero-field-cooled (ZFC) conductivities are larger than the field-cooled (FC) ones, which coincides with the hysteresis of $\kappa(H)$ curves. This difference indicates that there are less ferroelectric domains if the sample is cooled in zero field. From these data, one can get a rough estimation of the averaged distance between the ferroelectric domain walls, which usually has the same order of magnitude as that of the mean free path of phonons as long as the domain walls are effective phonon scatterers. Following the preceding calculation on the 14 T $\kappa(T)$ data, the mean free path of phonons is obtained to be 20–30 μm from the ZFC data in Fig. 5. This is a rather reasonable value of domain size for the ferroelectric single crystals.

Note that the hysteresis of $\kappa(H)$ of a magnetic material itself is not strange. The irreversibility has been known to often appear at the field-induced first-order magnetic transition, such as the spin-Peierls-to-AF order,[16] the liquid-gas-like transition in spin-ice compounds,[36] etc. However, the hysteretic $\kappa(H)$ of $GdFeO_3$ is somewhat different, because it appears in a rather broad field range where the magnetization does not show irreversibility.[24] In contrast, another well-known large hysteresis of low-T $\kappa(H)$ is the one observed in the high-T_c cuprate $Bi_2Sr_2CaCu_2O_8$ (BSCCO),[37,38] in which the hysteresis is well understood by the vortex-pinning effect that is accompanied with the irreversible macroscopic magnetization. From the preceding discussions, one can see that the irreversible $\kappa(H)$ of $GdFeO_3$ is most likely caused by the ferroelectric domain walls scattering on phonons, which is dependent on the history of applying the magnetic field. It should be pointed out that the phonon scattering by the ferroelectric domain walls had been studied by modifying the domain structure through applying the electric field directly.[39,40] It was proved in KH_2PO_4 that the low-T thermal conductivity of the single-domain state is much larger than that of the multidomain state.[39] Similar result was obtained in $SrTiO_3$, in which the low-T thermal conductivity under high electric field is clearly larger than that in zero field.[40] However, these former experiments should be analyzed very carefully because applying an electric field using the contacts on the sample surface could bring some uncertainties in the thermal conductivity measurements. In this regard, changing the domain structures by applying magnetic field is free from such problems and can give more reliable data. It is intriguing that in multiferroic $GdFeO_3$ the ferroelectric domain structures are able to be manipulated by the magnetic field, which is a key to making the peculiar low-T $\kappa(H)$ hysteresis observable.

IV. SUMMARY

The low-temperature heat transport of $GdFeO_3$ single crystal is found to be strongly dependent on the magnetic field and is helpful for studying the magnetic transitions and magnetoelectric coupling in this material. The magnons play an important role in the low-T thermal conductivity by scattering phonons instead of acting as heat carriers. As a result, both the spin flop or reorientation of the magnetic structure and spin polarization cause significant phonon scattering at the transition fields. The most remarkable result is that the low-T (<1 K) thermal conductivity shows an irreversible behavior on the history of applying the magnetic field. This phenomenon is rather peculiar in the sense that it appears in a broad range of magnetic field (~0–3 T) where the magnetization is known to be almost reversible. Furthermore, the hysteresis of $\kappa(H)$ or the irreversibility of ZFC and FC $\kappa(T)$ become larger upon lowering temperatures. All these data suggest that the ferroelectric domain structures, which are surprisingly sensitive to the history of applying the magnetic field, are playing the key role in producing the irreversibility of thermal conductivity through the phonon scattering by the domain walls. The present results show an interesting case that the ferroelectric domains of a multiferroic material can be manipulated by a magnetic field, and this kind of magnetoelectric coupling can be observed by the heat-transport measurement at very low temperatures.

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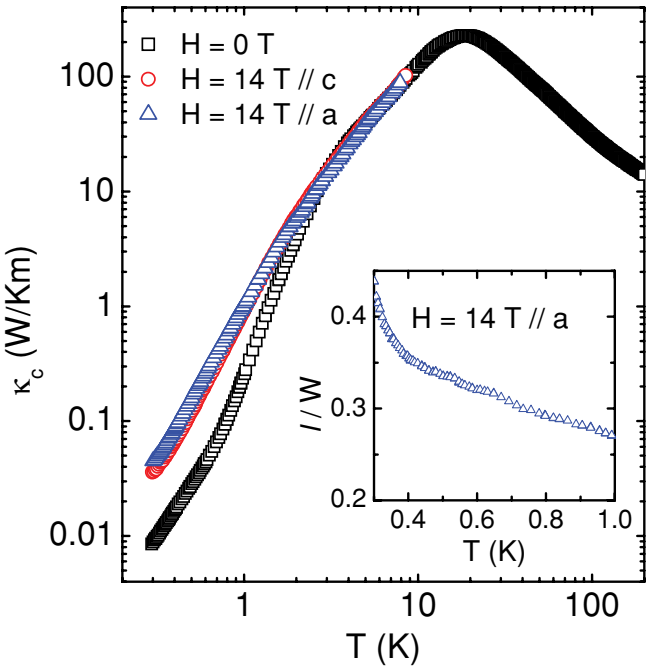

FIG. 6. (Color online) Temperature dependencies of the c-axis thermal conductivity of $GdFeO_3$ single crystal in zero and 14 T magnetic fields along the a or c axis. The inset shows the temperature dependence of the phonon mean free path l divided by the averaged sample width W (=0.344 mm) in 14 T magnetic field.

APPENDIX: THE c-AXIS THERMAL CONDUCTIVITY OF $GdFeO_3$

Figure 6 shows the temperature dependencies of κ_c for $GdFeO_3$ single crystals in zero and 14 T magnetic field parallel to the a and c axes. Apparently, these data are essentially the same as those of $\kappa_a(T)$, including all the main features like the magnitude of phonon peak, the weak-kink-like temperature dependence below ~2 K, the significant recovery of conductivity in the 14 T field, etc. In addition, the temperature dependencies of 14 T thermal conductivities are also similar to those of $\kappa_a(T)$ in 14 T. The calculated mean free path of phonons along the c axis is found to have the same order of magnitude as that from κ_a, as shown in the inset to Fig. 6. One can easily conclude that the phonon heat transport is nearly isotropic in $GdFeO_3$.

Figures 7(a) and 7(b) show the magnetic-field dependence of the c-axis thermal conductivity of $GdFeO_3$ single crystal. The overall behaviors of $\kappa_c(H)$ are qualitatively the same as those of $\kappa_a(H)$; that is, the thermal conductivity is suppressed at low fields and strongly enhanced at high fields. Moreover, at low fields there are also two dips for $H \parallel a$ and one dip for $H \parallel c$, respectively. One may note that the dip fields of κ_c for both $H \parallel a$ and $H \parallel c$ are somewhat different from those of κ_a when the field is applied along the same direction. However, such discrepancy is likely due to the demagnetization effect. Both samples have size about $2.5 \times 0.6 \times 0.15$ mm^3. For such kind of long-shaped samples, the demagnetization factor n is negligible ($\approx$0) when the applied field is along the longest dimension, while it is not negligible (taking a value between 0 and 1) when the field is along the shortest

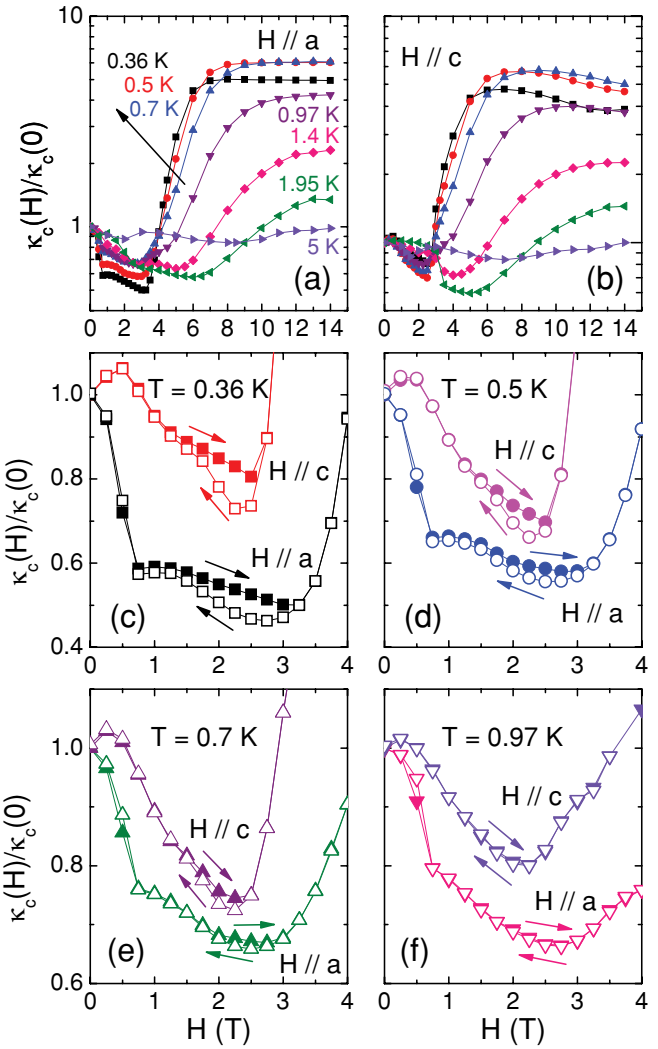

FIG. 7. (Color online) (a),(b) Magnetic-field dependencies of the c-axis thermal conductivity of $GdFeO_3$ single crystal. The magnetic fields are applied along the a or c axis and all the data are measured in the field sweeping-up process after zero-field cooling. (c)–(f) Low-field $\kappa_c(H)$ isotherms of $GdFeO_3$ single crystal at sub-Kelvin temperatures with magnetic field along the a and c axes. The solid symbols show data measured with ascending field after the sample is cooled in zero field, while the open symbols show the data with descending field, as indicated by arrows.

dimension. For the a-axis sample, its a axis is along the longest dimension and the c axis is along the shortest dimension; the c-axis sample has the c axis and a axis along the longest and the shortest dimensions, respectively. Therefore, for the experimental configurations of (κ_a, $H \parallel a$) and (κ_c, $H \parallel c$), the inner magnetic field (H_i) is equal to the external field (H) since $n \approx 0$; for the configurations of (κ_a, $H \parallel c$) and (κ_c, $H \parallel a$), the inner field is different from the external one and can be expressed as $H_i = H/(1 + n\chi)$, where χ is the magnetic susceptibility. Note that although the factor $(1 + n\chi)$ is not available for our samples, it is possible to make a comparison between $\kappa_a(H)$ and $\kappa_c(H)$ data taking into account the demagnetization effect. The comparison of the dip fields between $\kappa_a(H)$ and $\kappa_c(H)$ for both $H \parallel a$ and $H \parallel c$ indicated that the factor $(1 + n\chi)$ is about 1.5. For example, in the case

of (κ_a, $H \parallel a$) the dip fields of 0.5 and 2.25 T are intrinsic values of transition fields; the dip fields of 0.75 and 3.25 T in the case of (κ_c, $H \parallel a$) rescaled by the factor of 1.5 give values of 0.5 and 2.2 T, respectively, both of which match the dip fields of $\kappa_a(H)$ very well. Under such a consideration, it is a bit strange that the dip fields of (κ_a, $H \parallel c$) and (κ_c, $H \parallel c$) do not differ much from each other. Therefore, a quantitative analysis of these data is called for.

The $\kappa_c(H)$ isotherms for both $H \parallel a$ and $H \parallel c$ also present the hysteresis on the magnetic field sweeping up and down, as shown in Figs. 7(c)– 7(f). It can be seen that the field region and temperature regime for showing the hysteresis, the difference between the field up and down data, are all very similar to those of $\kappa_a(H)$ data. Apparently, these results have the same origin as those of $\kappa_a(H)$.

Figure 8 shows the magnetic-field-induced irreversibility of $\kappa_c(T)$, measured in some characteristic fields by warming up the sample after zero-field cooling or field cooling to the lowest temperature. They also show similar behaviors to those of the ZFC and FC $\kappa_a(T)$ data.

In summary, the low-T heat transport of $GdFeO_3$ is nearly isotropic. There is strong coupling between the phonons and magnons, which determines the main features of the magnetic-field dependence of thermal conductivity. The characteristic transitions of $\kappa(H)$ isotherms are strongly dependent on the direction of external field and are caused by the field-induced transitions of magnetic structure. An irreversibility of low-T thermal conductivity on the magnetic field is observed and is likely due to the phonon scattering by the ferroelectric domain walls. The peculiarity is that this phenomenon points to the manipulation of ferroelectric properties by magnetic field, which is a characteristic of multiferroic materials.

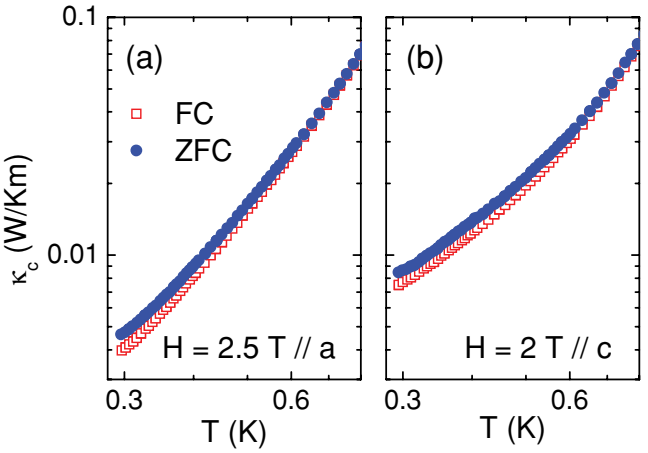

FIG. 8. (Color online) Temperature dependencies of the c-axis thermal conductivity of $GdFeO_3$ single crystal in 2.5 T magnetic field along the a axis (a) and in 2 T field along the c axis (b). The data are taken while slowly warming up the sample from the lowest temperature after field cooling or zero-field cooling.

*xfsun@ustc.edu.cn

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