Flux growth and physical properties of Mo₃Sb₇ single crystals

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Millimeter sized single crystals of Mo₃Sb₇ are grown using the self-flux technique and a thorough characterization of their structural, magnetic, thermal, and transport properties is reported. The structure parameters for the high-temperature cubic phase and the low-temperature tetragonal phase were, for the first time, determined with neutron single crystal diffraction. Both X-ray powder diffraction and neutron single crystal diffraction at room temperature confirmed that Mo₃Sb₇ crystallizes in Ir₃Ge₇-type cubic structure with space group Im3m. The cubic-tetragonal structure transition at 53 K is verified by the peak splitting of (400) reflection observed by X-ray single crystal diffraction and the dramatic intensity change of (12 0 0) peak observed by neutron single crystal diffraction. The structural transition is accompanied by a sharp drop in magnetic susceptibility, electrical resistivity, and thermopower while cooling. A weak lambda anomaly was also observed around 53 K in the temperature dependence of specific heat and the entropy change across the transition is estimated to be 1.80 J/molMo.K. The temperature dependence of magnetic susceptibility was measured up to 750 K and it follows a Curie-Weiss behavior above room temperature. Analysis of the low-temperature magnetic susceptibility suggests a spin gap of 110 K around 53 K. A typical phonon thermal conductivity was observed in the low temperature tetragonal phase. A glassy phonon thermal conductivity above 53 K suggests a structural instability in a wide temperature range. Superconductivity was observed at 2.35 K in the as-grown crystals and the dimensionless specific heat jump \( \Delta C(T)/\gamma_n T_c \) was determined to be 1.49, which is slightly larger than the BCS value of 1.43 for the weak-coupling limit.

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INTRODUCTION

Despite a relatively low superconducting transition temperature \( T_c = 2.08 \text{ K} \), [1] the Zintl compound Mo₃Sb₇ has attracted considerable interest due to the possible involvement of magnetism in superconducting pairing,[2–5] and promising thermoelectric performance with proper doping.[6–9] Mo₃Sb₇ is the only known compound in the Mo-Sb binary system. It crystallizes in a Ir₃Ge₇-type cubic structure with space group Im3m at room temperature. The Mo-sublattice is characterized by a three dimension network of Mo-Mo dumbbells formed by nearest neighbours (NN) and octahedral cages at the body center positions formed by next nearest neighbors (NNN). The competition between strong antiferromagnetic NN and NNN interactions is proposed to drive a structure transition at \( T^* = 53 \text{ K} \) from cubic to tetragonal (space group I4/mmm) to relieve spin frustration.[10–12] This structure transition further shortens the NN Mo-Mo distance along the crystallographic c-axis and forms spin singlet dimers. μSR, inelastic neutron scattering, and magnetic susceptibility measurements on polycrystalline samples suggest that the formation of a 120 K spin gap accompanies the structural transition upon cooling.[3, 4] With a structure transition and a spin gap above \( T_c \), Mo₃Sb₇ is a unique system for exploring the interplay between magnetism, structure instability, and superconductivity.

Despite much effort, the pairing mechanism at low temperatures and the correlation between the structural transition, magnetic frustration, and superconductivity are still controversial. Thorough studies of the intrinsic properties of Mo₃Sb₇ and related compounds have been hampered by the unavailability of sizable single crystals. The first attempt to grow Mo₃Sb₇ single crystals was performed by chemical transport reactions and resulted in small crystals adequate for determining the crystal structure.[13] Millimeter sized single crystals suitable for some physical property measurements were first grown by melting Sb in a thick Mo tube.[1] Upon cooling from 1000°C to 700°C at the rate of 3°C/h, single crystals grew on the walls of the Mo tube. Crystals grown in this manner become superconducting at \( T_c = 2.08 \text{ K} \), and enabled several studies of the intrinsic properties.[1, 14, 15] However, these crystals are still small in size. More importantly, it’s difficult to grow crystals doped with other elements, especially substitutions at the Mo site.

In this paper, we report the flux growth of millimeter sized Mo₃Sb₇ single crystals and a thorough characterization of the crystals by x-ray powder diffraction, x-ray and neutron single crystal diffraction, magnetic susceptibility, electrical resistivity, thermoelectric power, thermal conductivity, and specific heat measurements. Crystals grown by the self-flux technique posses the highest \( T_c \) reported to date and are free of magnetic impurities. Neutron single crystal diffraction was performed, for
the first time, to determine the structure parameters of the cubic phase at room temperature and the tetragonal phase at 4 K. The structural transition is accompanied with anomalies in the temperature dependence of electrical resistivity, magnetization, specific heat, thermopower and thermal conductivity.

EXPERIMENTAL DETAILS

Single crystals of MoSb7 were grown out of Sb flux. The starting materials are elemental Mo powder (Alfa, 99.999%) and Sb (Alfa, 99.9999%). Mo powder was first reduced in flowing Ar balanced with 4% H2 for 12 hours at 1000°C. Reduced Mo powder and commercial Sb shot were mixed in the ratio of Mo:Sb = 1:49 and placed in a 2 ml Al2O3 crucible. A catch crucible of the same size containing quartz wool was mounted on top of the growth crucible and both were sealed in a silica ampoule under approximately 1/3 atmosphere of argon gas. The sealed ampoule was heated to 1000°C in 5 hours and homogenized for 12 hours before cooling to 700°C over 100 hours in a programmable box furnace. At 700°C, the Sb flux was decanted from the MoSb7 crystals.

Elemental analysis of the crystals was performed using a Hitachi TM-3000 tabletop electron microscope equipped with a Bruker Quantax 70 energy dispersive x-ray system. X-ray diffraction from oriented single crystals and from powders ground from crystals was performed on PANalytical X’Pert Pro MPD powder x-ray diffractometer using Cu Kα1. The room temperature x-ray powder diffraction pattern was refined by the Rietveld method using Fullprof.[16] Single crystal neutron diffraction was measured at HB-3A four-circle diffractometer at the High Flux Isotope Reactor at the Oak Ridge National Laboratory. A neutron wavelength of 1.003 Å was used with a bent perfect Si-331 monochromator.[17] The data were refined by the Rietveld method using Fullprof. Magnetic properties were measured with a Quantum Design (QD) Magnetic Properties Measurement System (MPMS) in the temperature interval 1.8 K ≤ T ≤ 750 K. The temperature dependent specific heat and electrical transport data were collected using a 14 Tesla QD Physical Properties Measurement System (PPMS) in the temperature range of 1.9 K ≤ T ≤ 300 K. Thermal conductivity and thermopower were measured from 1.9 K to 300 K using the Thermal Transport Option (TTO) from QD and a 9 Tesla PPMS. A rectangular bar with the dimension of 0.6 mm × 0.7 mm × 6 mm was cut from a large crystal and used for the TTO measurement. Silver epoxy (H20E Epo-Tek) was utilized to provide mechanical and thermal contacts during the thermal transport measurements.

RESULTS AND DISCUSSIONS

Crystal growth and phase stability

As-grown crystals are normally cube-like with truncated corners as shown in the inset of Fig. 1. The typical dimension of a crystal is about 2-3 mm. Elemental analysis confirmed that the crystals are stoichiometric MoSb7 with no observable deviation. Figure 1 shows the x-ray powder diffraction (XRD) data collected on ground MoSb7 single crystals. The XRD data were analyzed by Rietveld refinement using the FullProf software and the Rietveld fit profiles are also presented in Fig. 1. The XRD data indicate that the crushed crystals are single phase MoSb7. Weak reflections from Sb were observed in some measurements. This small amount of Sb is from residual flux on the surface of the crystals after the decanting and can be removed mechanically or by heating the crystals in evacuated and sealed quartz tube at 600°C with the cold end at room temperature.

Growths with various charge/flux ratios were performed in order to optimize the growth and the yield. We noticed that raising the charge to flux ratio or cooling faster leads to smaller MoSb7 crystals. No sizeable crystals were obtained using the above process once the Mo content is over 5 at%, even with a 24-hour homogenization at 1150°C before cooling. From the presently available phase diagram,[18] MoSb7 decomposes at 780°C into (Mo) and liquid (Sb). However, a test growth stopped at 800°C also yields MoSb7 crystals from a Mo:Sb=1:49 melt. This suggests that there is a wide temperature and composition range where MoSb and liquid (Sb) coexist. However, the liquidus temperature
should increase rapidly with increasing Mo content in the melt, which limits the charge/flux ratio during crystal growth. A Mo/Sb ratio of 1:49 has been found to reproducibly grow the largest crystals.

Structure

The Rietveld refinement of the x-ray powder data shown in Fig. 1 confirmed that as-grown Mo₃Sb₇ single crystals crystallize in the Ir₃Ge₇ type structure with the cubic Im3m (space group 229) symmetry at room temperature. The room temperature structure is further confirmed by a single crystal neutron diffraction measurement. Table 1 shows the crystallographic parameters refined for the room temperature x-ray powder diffraction pattern and the neutron single crystal diffraction data. The results agree well with each other and previous reports.[11, 12]

A structural transition from cubic to tetragonal was reported to take place at 53 K in polycrystalline samples. Single crystal x-ray and neutron diffraction were used to study this transition in our crystal. Figure 2 shows the evolution of the cubic (400) peak with temperature from 11 K to 100 K. Below 54 K, the peak splits signaling the lowering of the symmetry. At 11 K, the a/c ratio was obtained to be 1.002, consistent with previous reports from powder x-ray diffraction.[11, 12]

Figure 3 shows the temperature dependence of the integrated intensity of the cubic (120 0) reflection measured by neutron single crystal diffraction on a Mo₃Sb₇ single crystal. Inset shows the peak splitting and the fitting of low temperature peaks.

Superconducting transition

Superconductivity is observed to occur below Tc = 2.35 K, as indicated by the magnetization, electrical resistivity, and specific heat data shown in Fig. 4. Magnetization was measured in both zero-field-cooling (ZFC) and field-cooling (FC) modes with an applied magnetic field of 10 Oe. The observed diamagnetism shown in Fig. 4(a) confirms bulk superconductivity. The onset of the superconducting transition temperature is ~2.35 K, which agrees well with that determined from the temperature dependence of resistivity (also shown
TABLE I: Structure parameters for Mo$_3$Sb$_7$ with the space group Im$\overline{3}m$ (no. 229) at room temperature. Atomic coordinates are: Mo (x,0,0), Sb1 (0.25,0.5,0.5), and Sb2 (x,x,x). X-ray data were obtained from Rietveld refinement of powder diffraction pattern collected on pulverized single crystals. Neutron data were measured on a piece of single crystal of 30 mg at HB-3A. Lattice parameter a was determined to be 9.569(2) Å by x-ray and 9.543(2) Å by neutron diffraction.

| atom | site | x (Xray/Neutron:X/N) | U$_{iso}$(Å$^2$)(X/N) |
|------|------|----------------------|------------------------|
| Mo   | 12e  | 0.3438(3)/0.34340(16) | 0.0060(3)/0.0041(5)    |
| Sb1  | 12d  | 1/4                  | 0.0084(3)/0.0068(5)    |
| Sb2  | 16f  | 0.16268(9)/0.16219(10)| 0.0081(3)/0.0055(4)    |

TABLE II: Structure parameters for Mo$_3$Sb$_7$ with the space group I4/mmm (no. 139) at 4 K. Neutron data were measured on a piece of single crystal of 30 mg at HB-3A. The lattice parameters are a = 9.551(4) Å, and c = 9.523(2) Å with a/c = 1.003. R$_F$ = 0.0373, $\chi^2$ = 3.563 for 210 F$_o$ > 2s(F$_o$).

| atom | site | x | y | z | U$_{iso}$(Å$^2$) |
|------|------|---|---|---|-----------------|
| Mo1  | 8i   | 0.3437(2) | 0  | 0  | 0.0016(6)       |
| Mo2  | 4e   | 0  | 0  | 0  | 0.0012(9)       |
| Sb1  | 4d   | 0  | 1/2| 1/4| 0.0013(11)      |
| Sb2  | 8j   | 0.2501(6) | 1/2| 0  | 0.0012(6)       |
| Sb3  | 16m  | 0.16232(13)| 0.16232(13)| 0.1621(3)| 0.0010(4) |

in Fig 4(a)). Figure 4(b) shows the low temperature specific heat data plotted as $C_p/T$ vs. $T^2$. A specific heat jump at $2.35 \pm 0.05$ K was well resolved at the onset of superconductivity. High magnetic fields (>2 T) suppress superconductivity and the specific heat jump disappears as shown in Fig. 4(b). Literature values of $T_c$ vary from 2.02 K to 2.30 K, with the variation likely coming from sample quality.[2, 14, 15, 20] The current as-grown crystals posses the highest $T_c$ reported to date.

The fitting of specific heat data in the range $8 < T^2 < 60$ K$^2$ to the standard power law, $C_p/T = C_p/T^2$ yields $\gamma = 31.8(2)$ mJ/mol K$^2$ and $\beta = 0.64(1)$ mJ/mol K$^4$, where $\gamma$ is the Sommerfeld electronic specific heat coefficient and $\beta$ the coefficient of the Debye $T^3$ lattice heat capacity at low temperatures. The latter gives the Debye temperature $\theta_D$ with the following relation $\theta_D = (12\pi^4 N_A k_B T/\beta)^{1/3}$, where $n$ is the number of atoms per formula unit, $N_A$ is Avogadro’s constant and $k_B$ is Boltzmann’s constant. With $n = 10$ and $\beta = 0.64(1)$ mJ/mol K$^4$, the Debye temperature is $\theta_D = 248$ K for Mo$_3$Sb$_7$. We note that the Debye temperature is similar to that reported by Candolli et al.[2] but is smaller than that reported by Tran et al.[3, 21] The dimensionless specific heat jump $\Delta C(T)/\gamma_n T_c$ was determined to be 1.49, close to 1.56 reported by Tran et al.[21] This value is slightly larger than the BCS value of 1.43 for the weak-coupling limit.

The density of states at the Fermi level $D(E_F)$ can be obtained from the Sommerfeld coefficient $\gamma$ according to:

$$\gamma = \frac{\pi^2 k_B^2}{3} D(E_F)(1 + \lambda_{e-\phi})$$

where $\lambda_{e-\phi}$ is the electron-phonon coupling constant and could be estimated with the McMillan equation:

$$\lambda_{e-\phi} = \frac{1.04 + \mu^* \ln(\theta_D/1.45 T_c)}{(1 - 0.62 \mu^* \ln(\theta_D/1.45 T_c) - 1.04)}$$

where $\mu^*$ is the Coulomb pseudopotential and usually taken between 0.1 and 0.15. With $\mu^* = 0.15$, $\Theta_D = 248$ K, and $T_c = 2.35$ K, $\lambda_{e-\phi}$ is 0.59 consistent with a previous report.[21] The density of states at the Fermi level $D(E_F)$ is calculated to be 8.5 states/eV f.u., where f.u. means formula unit. The value is comparable to that obtained by theoretical calculations.[22]

Physical properties in normal state

Figure 5 shows the temperature dependence of the magnetic susceptibility, $\chi(T)$, measured with an applied field of 60 kOe in the temperature range 2 K $\leq$ T $\leq$ 750 K. For $\chi(T)$ measured above room temperature, the contribution from the sample holder was appropriately corrected. With decreasing temperature, $\chi(T)$ increases and shows a broad maximum around $T_{max} = 175$ K which is followed by a sharp drop around 50 K. The sharp drop is best illustrated by the derivative $d\chi/dT$, which shows a distinct maximum around 50 K as shown in inset of Fig. 5. The features below room temperature agree with previous reports.[2, 3] It’s noteworthy that below 20 K $\chi(T)$ shows negligible temperature dependence. While in all previous reports on the magnetic properties of polycrystalline samples, a Curie-Weiss (CW)-like tail is observed below 50 K, which has been attributed to unpaired spins. The absence of the CW-like tail further confirms the high quality of our crystals. The isothermal magnetization
FIG. 4: (color online) (a) The temperature dependence of magnetic susceptibility (left) measured in both zero-field-cooling (ZFC) and field-cooling (FC) modes with a field of 10 Oe and electrical resistivity (right). (b) The low-temperature specific heat of Mo$_3$Sb$_7$ single crystal divided by temperature as a function of temperature square measured in both zero-field and field of 60 kOe in the temperature range 2 K ≤ T ≤ 750 K. The solid lines are guide to the eye. The dashed line is the linear fitting of the low temperature specific heat as described in the text.

FIG. 5: (color online) The temperature dependence of magnetic susceptibility of Mo$_3$Sb$_7$ single crystal measured under a magnetic field of 60 kOe in the temperature range 2 K ≤ T ≤ 750 K. The solid curve below 50 K shows the fitting as described in text. The lower inset shows the temperature derivative of magnetic susceptibility, dχ(T)/dT. The upper inset shows the linear fitting of χ(T)$^{-1}$. The solid curve below 50 K shows the fitting as described in text. The lower inset shows the temperature derivative of magnetic susceptibility, dχ(T)/dT. The upper inset shows the linear fitting of χ(T)$^{-1}$.

(Not shown) measured at 5 K and room temperature indicates no ferromagnetic component.

As shown in Fig. 5, χ(T) below 50 K was fit with a spin gap function χ(T) = χ(0) + bexp(−Δ/kB T), where χ(0) is a temperature independent term, b is a constant, Δ is the spin gap, kB is the Boltzmann constant. The best fitting was obtained with the following parameters: χ(0) = 3.7 × 10$^{-4}$ cm$^3$/mol, b = 5.8 × 10$^{-4}$ cm$^3$/mol, and Δ/kB = 110(6) K. The gap is similar to that reported on polycrystalline samples.[3]

The magnetic susceptibility of Mo$_3$Sb$_7$ in the temperature interval 220 K ≤ T ≤ 300 K has been reported[3] to follow Curie-Weiss law. The upper inset of Fig. 5 shows the linear fitting of χ(T)$^{-1}$ above 300 K. The fitting yields θ = −1078 K and μeff S=1/2. The effective magnetic moment is close to the expected value for Mo ions with S=1/2. While such a large negative Weiss constant suggests strong antiferromagnetic interaction between localized Mo moments.

Figure 6 shows the temperature dependence of electrical resistivity in the temperature range 3 K ~ 300 K. The electrical resistivity at room temperature is about 160 µΩ.cm. As highlighted by the solid line in the Figure, at temperatures above ~150 K, the electrical resistivity shows a linear temperature dependence consistent with the report by Bukowski et al.[1] Starting around 50 K, the electrical resistivity shows a sharp drop. This sharp drop can be better illustrated by the derivative of the electrical resistivity shown in the upper inset. At even lower temperatures, the resistivity levels off with cooling and finally drops to zero at T$_c$. The low temperature electrical resistivity in polycrystalline samples has been found to fit a ρ(T) = ρ$_0$ + cT$^2$ law with n around 2.4, which has been observed when fitting ρ(T) measured on crystals from different batches. We also tried to fit the low temperature electrical resistivity with a gap function ρ(T) = ρ$_0$ + cT + dexp(−Δ/2kBT) which has been used to argue against the spin fluctuation scenario and point to a gap feature.[3] As shown in the lower inset of Fig. 6, a good fit could be obtained with ρ$_0$ = 91.5 µΩ.cm, c = 5.58 × 10$^{-8}$ Ω.cm.K$^{-1}$, d = 9.36 × 10$^{-7}$ Ω.cm, and Δ/2kB = 147(2) K. The temperature independent magnetic susceptibility below 20 K and the absence of a quadratic temperature dependence of electrical resistivity below 50 K are inconsistent with
the existence of spin fluctuations in the normal state.

Figure 7 shows the temperature dependence of the specific heat, $C_p(T)$, measured under 0 T and 12 T applied magnetic fields. The magnetic field of 12 T suppresses superconductivity and the specific heat jump at $T_c$ disappears and the details were shown in Fig. 4(b). The heat capacity at 200 K attains a value of 226 J/mol K, which is a little smaller than the classical high temperature Dulong-Petit value of $3nR = 249$ J/mol K at constant volume, where $R$ is the molar gas constant and $n = 10$ is the number of atoms per formula unit. This agrees with the determined Debye temperature, which is slightly below room temperature. The inset of Fig. 7 highlights the details around 50 K. A weak lambda anomaly is well resolved around $T = 53$ K. No field dependence was observed for this anomaly with magnetic fields up to 12 T.

In order to estimate the entropy change around 53 K, we subtracted the lattice contribution to the specific heat using Ru$_3$Sn$_7$ as a reference. Figure 7 (b) shows the residual specific heat plotted as $\Delta C_p/T$ vs $T$. The entropy change, which is calculated as $\int \Delta C_p/T \, dT$, is 1.80 J/molMo K. As illustrated in Fig. 7(b), about 60% entropy change takes place above 53 K.

Figure 8 shows the evolution of the thermopower, $\alpha(T)$, with temperature. A room temperature value of $\sim 16\mu$V/K agrees with the measurement on a polycrystalline sample. Above 100 K, $\alpha(T)$ shows a nearly linear temperature dependence. Below about 60 K, $\alpha(T)$ decreases quickly when cooling; this sharp drop resembles that in the temperature dependence of electrical resistivity around 53 K. Below 30 K, $\alpha(T)$ stays around zero. It’s interesting to note that $\rho(T)$ levels off and is nearly temperature independent below 30 K. The thermopower is proportional to the logarithmic derivative of the density of states (DOS) with respective to energy at the Fermi level, while the electrical conductivity increases with DOS. The observed change of $\alpha(T)$ and $\rho(T)$ suggests an electronic structure change across the structure transition.

Figure 9 shows the temperature dependence of the thermal conductivity in the normal state. With decreasing temperature, the thermal conductivity decreases from room temperature down to 50 K; below 50 K, a maximum near 20 K was observed. Since no long range magnetic order was observed in Mo$_3$Sb$_7$, possible heat carriers are electrons and phonons. Thus the total thermal conductivity can be described as: $\kappa_{\text{total}} = \kappa_e + \kappa_p$, where $\kappa_e$ is the electronic thermal conductivity, and $\kappa_p$ the lattice thermal conductivity. $\kappa_e = L T/\rho$, where $L$ is the Lorenz constant taken to be equal to $2.44 \times 10^{-8} \text{ V}^2/\text{K}^2$, $T$ is the absolute temperature, and $\rho$ is the electrical resistivity.
FIG. 8: (color online) The temperature dependence of thermopower of Mo$_3$Sb$_7$ single crystal. The dashed line is zero line.

FIG. 9: (color online) The temperature dependence of thermal conductivity of Mo$_3$Sb$_7$ single crystal. See the text for the calculation of electron and phonon thermal conductivities.

SUMMARY

Mo$_3$Sb$_7$ single crystals were successfully grown out of Sb flux. Our growth study suggests that there is a wide temperature and composition range where Mo$_3$Sb$_7$ and liquid (Sb) coexist. The sizeable crystals enabled the first neutron single crystal diffraction study of the high temperature cubic phase and the low temperature tetragonal phase. The physical properties are generally in line with previous reports on polycrystalline samples. However, the following features are noteworthy: (1) Magnetization, electrical resistivity and specific heat measurements observed superconductivity at $T_c = 2.35 \pm 0.05$ K in the as-grown crystals, which is the highest $T_c$ reported to date for Mo$_3$Sb$_7$. The corresponding dimensionless specific heat jump $\Delta C(T)/nT_c$ was determined to be 1.49, which is slightly larger than the BCS value of 1.43 for the weak-coupling limit. (2) A weak lambda anomaly was observed at 53 K in the temperature dependence of specific heat and no field effect was observed with magnetic field up to 12 T. The entropy change across the transition is estimated to be 1.80 J/molMo K and 60% entropy change takes place above 53 K. (3) The magnetic susceptibility shows negligible temperature dependence below $\sim$20 K suggesting the crystals are free of magnetic impurities. Above room temperature, the magnetic susceptibility follows CW law and a moment of 1.67 $\mu_B$/Mo is close to the expected value for Mo ions with spin $S = 1/2$. Thus the electronic state of Mo has both localized and itinerant characters. (4) The electrical resistivity below 50 K doesn’t show a quadratic temperature dependence.

the temperature dependence of $\kappa_e$ and $\kappa_p$; the latter was obtained by subtracting $\kappa_e$ from the total thermal conductivity. $\kappa_e$ decreases while cooling in the whole temperature range studied. We noticed that $\kappa_p$ is rather low in the whole temperature range. This might be due to large number of heavy atoms in the primitive unit cell or strong electron-phonon scattering. The maximum near 20 K for $\kappa_p$ is typical for a crystalline material though the maximum occurs at a low value. The striking feature for $\kappa_p$ is a glassy behavior above 53 K where the structure transition takes place. This kind of phonon glass behavior has been observed in a wide variety of materials, such as RVO$_3$,[24] RCoO$_3$,[25] La$_4$Ru$_2$O$_{10}$,[26] and filled skutterudite antimonides.[27] In the oxides with localized electrons, bond-length fluctuations induced by spin and/or orbital fluctuations disturb the phonon thermal conductivity through spin-orbital-lattice coupling. While in filled skutterudite antimonides, the rattling mode seriously damps the lattice vibration. We note that neutron single crystal diffraction didn’t observe abnormal atomic displacement parameters for either Mo or Sb in Mo$_3$Sb$_7$.[28] Thus, the phonon glass behavior of Mo$_3$Sb$_7$ might signal the effect of the structural instability resulting from the competing NN and NNN magnetic interactions. The cubic-tetragonal structural transition relieves the magnetic frustration thereby recovering the phonon heat transport in the tetragonal phase. This might be further enhanced by the reduced spin scattering due to the accompanied spin gap opening.
Analysis of the transport and magnetization data suggests the opening of a spin gap of 110 K accompanying the structure transition. A phonon glass behavior was observed above 53 K suggesting strong scattering of phonons by lattice instabilities. The abrupt change around 53 K in the temperature dependence of electrical resistivity and thermopower suggests an electronic structure change across the structural transition.

The sizeable high quality single crystals allow studies of intrinsic properties of Mo$_3$Sb$_7$. Moreover, preliminary growths have demonstrated that crystals with various substitutional dopants, for either Mo or Sb, can be grown with controlled doping using the reported growth protocol. This enables various future studies that will explore the relationship between the structure instability, magnetism and superconductivity, and the origin of the promising thermoelectric performance of doped Mo$_3$Sb$_7$.

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