Unusually Strong Orbit-Lattice Interactions in the RVO$_3$Perovskites

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The thermal conductivity $\kappa(T)$ of the RVO$_3$ crystals was measured. At $T > T_\infty$, RVO$_3$ crystals conduct heat like a glass; the phonon contribution to $\kappa(T)$ is completely suppressed by spin and orbital fluctuations. In the interval $T_N < T < T_\infty$, it is only partially restored by the orbital ordering due to spin fluctuations. In contrast with the amorphouslike $\kappa(T)$ at $T > T_\infty$, a phononlike $\kappa(T)$ was observed at $T < T_N$. This study shows clear-cut evidence of strong orbit-lattice coupling in RVO$_3$ perovskites. Thermal conductivity measurement could be used as a sensitive probe to study orbital ordering.

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The V(III) : $3d^2$ configuration in an octahedral site of an oxoperovskite is localized; the two electrons occupy a threefold-degenerate, π-bonding t-orbital manifold with azimuthal orbital angular momentum $m_l = 0, \pm 1$. A cooperative orbital ordering below a transition temperature T_∞ introduces a local site distortion to tetragonal symmetry; a site $c/a > 1$ reduces the orbital angular momentum whereas a $c/a < 1$ enhances it [1]. The orthorhombic RVO$_3$ perovskites all order antiferromagnetically below a T_N, and they have exhibited an intriguing sequence of orbital and magnetic orderings as is shown in Fig. 1 [2–7]. For R = Pr, Nd, ..., Lu, and Y, a second-order transition at a $T_\infty > T_N$ orders empty yz orbitals alternatively with empty zx orbitals on neighboring VO$_{6/2}$ sites to give a G-type orbital order. The antiferroic tetragonal ($c/a > 1$) site distortions are achieved by cooperative shifts of the O^{2-} ions of a (001) plane away from one V(III) neighbor toward the other; the shifts on alternate (001) planes are out-of-phase. In accordance with the Goodenough-Kanamori rules for the sign of the V-O-V spin-spin interactions, this G-type orbital order gives, below T_N, a type-C antiferromagnetic order in which ferromagnetic c-axis chains couple antiferromagnetically to one another. However, for R = Dy, ..., Lu, and Y, a first-order orbital reordering transition occurs at a T_{CG}; below T_{CG}, the oxygen displacements in the alternate (001) planes become in-phase, which results in C-type orbital order and type-G antiferomagnetic order. The space group changes from orthorhombic Pbnm for $T > T_\infty$ and $T < T_{CG}$ to monoclinic $P2_1/n$ in the interval $T_{CG} < T < T_\infty$. A $T_N > T_\infty$ and a first-order transition at T_∞ have been reported for LaVO$_3$ [5]. However, (T_N-T_∞) is only a few degrees and no definitive investigation of a possible cooperative site distortion in the interval $T_\infty < T < T_N$ has been made. Whether the orbitals are ordered and how the spins are coupled in the small temperature interval $T_\infty < T < T_N$ has been a subject of debate. With respect to CeVO$_3$, a similar $T_N > T_\infty$ has also been reported [4,6,8]. However, a recent synchrotron diffraction study [5] on high quality single crystals suggests $T_\infty > T_N$ as in other RVO$_3$ (R = Pr, ... Lu) members.

In this Letter, we study the variation of the thermal conductivity $\kappa(T)$ of RVO$_3$ crystals with the motivation of probing the lattice dynamics associated with these transitions. Of particular interest is the observation that in the orbitally disordered paramagnetic phase, RVO$_3$ crystals conduct heat like a glass; phonon thermal conductivity is only partially restored in the paramagnetic interval $T_N < T < T_\infty$. We also consider whether orbitons contribute to $\kappa(T)$ below T_∞. The symmetry breaking associated with an ordered state is always accompanied by the creation of new quasiparticles as is illustrated by magnons in a magnetically ordered phase. The orbiton would be the quasiparticle in an orbitally ordered phase. Saitoh *et al.* [9] have claimed identifying orbitons by Raman scattering in LaMnO$_3$. However, the orbital order-disorder transition temperature $T_{JT} = 750$ K is too high for a convenient and precise check of the lattice dynamics with a $\kappa(T)$ measurement. In the RVO$_3$ perovskites, T_∞ is low enough to perform such a check, but the temperature appears to be too low for thermal excitation of the orbiton.

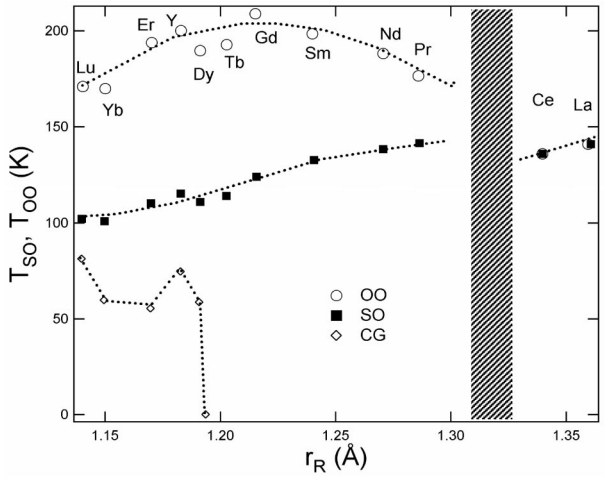

FIG. 1. Spin-orbital phase diagram of RVO$_3$ perovskites redrawn from Ref. [4].

Samples were melt-grown from polycrystalline RVO_3 rods with an IR image furnace in an atmosphere of Ar + 5% H_2. Polycrystalline RVO_3 samples were obtained by reducing RVO_4 powder in flowing H_2 at 1000°C with intermittent grinding. The RVO_4 powders were prepared by standard solid-state reaction method. About 5% extra V_2O_5 in the feed rod proved necessary to compensate evaporation loss and to stabilize the molten zone. Since their melting points are close to the upper limit of our image furnace, the crystal quality of $LaVO_3$ and $CeVO_3$ was relatively poor in comparison with other members in this family. All samples were annealed at 850°C for 5 h to relieve the stress formed during crystal growth before the thermal conductivity was measured. All samples were single-phase to powder x-ray diffraction and the room-temperature peaks could be indexed with the orthorhombic Pbnm space group. The cell volume increases monotonically with increasing R^{3+}-ion size. Oxygen stoichiometry was monitored by thermoelectric-power measurements and by thermogravimetric analysis (TGA). Thermal conductivity was measured by a steady-state method as reported elsewhere [10]. Magnetic susceptibility $\chi(T)$ was obtained with a SQUID magnetometer; measurements were made with either cooling in 1 kOe (FC) or on heating in 1 kOe after cooling in zero-field (ZFC).

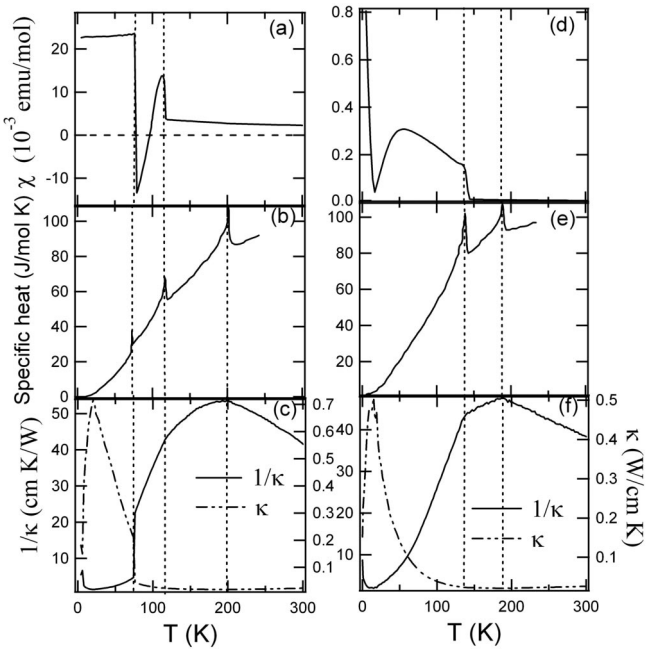

FIG. 2. Temperature dependence of magnetic susceptibility, specific-heat from Ref. [4], and thermal conductivity for YVO_3 (a), (b), (c) and $NdVO_3$ (d), (e), (f). Magnetic susceptibility was measured at 1 kOe in a field-cooling (FC) mode. Vertical dashed lines indicate the transition temperatures T_∞, T_N, and T_{CG}.

Figure 2 compares the thermal conductivity $\kappa(T)$ with the specific-heat $C_p(T)$ from Ref. [4] and magnetic susceptibility $\chi(T)$ of $NdVO_3$ and YVO_3. These two compositions were chosen to be representative of the two classes of RVO_3 (R = Pr, Nd, ..., Lu, and Y) perovskites as distinguished in Fig. 1 by whether a first-order transition occurs at a T_{CG}. The specific-heat data show a first-order anomaly at T_{CG} and second-order lambda anomalies at T_∞ and T_N. The $\chi(T)$ data show an abrupt appearance of a weak ferromagnetism on cooling through T_N and only a gradual slope change around T_∞. In addition, the first-order transition at T_{CG} in YVO_3 is marked by an abrupt change of sign of the weak ferromagnetism in the $\chi(T)$ curve. T_∞, T_N, and T_{CG} defined from the magnetic susceptibility of our samples are consistent with those defined from the specific-heat data. These measures of T_∞, T_N, and T_{CG} allow a study of how heat transfers in the different phases marked by the critical temperatures.

Two prominent features of the thermal conductivity are worthy of special note: (1) At T_∞ and T_N defined by magnetization and specific-heat, there is an obvious change of slope of $1/\kappa(T)$, indicating a change of scattering mechanism and/or degree of scattering for heat carriers; $\kappa(T)$ of YVO_3 shows a steplike jump at $T_{CG} = 77$ K. (2) More striking is the observation that above T_∞, $\kappa(T)$ shows a positive temperature dependence typical of heat transport in an amorphous solid. The slope changes and the steplike jump take place at temperatures coinciding with T_∞, T_N, and T_{CG}, respectively. This coincidence can only be explained by the onset of orbital and spin order. Therefore, we can understand the temperature dependence of $\kappa(T)$ for $NdVO_3$ and YVO_3 as follows: (1) In an orbitally disordered paramagnetic state, $\kappa(T)$ shows a glassy behavior. (2) Orbital order revives partially the phonon thermal conductivity in the paramagnetic phase. (3) Spin ordering further restores κ_{ph} in the orbitally ordered antiferromagentic state where $\kappa(T)$ demonstrates a typical phonon behavior. (4) The steplike jump in $\kappa(T)$ curve at T_{CG} indicates that the orthorhombic phase with type-G magnetic order is more thermally conductive than the monoclinic phase with type-C magnetic order.

Since all interesting transitions occur at $T > 70$ K where thermal conductivity is small, a curve of $1/\kappa$ versus T is plotted in Fig. 3 to highlight the features at high temperatures. The $1/\kappa(T)$ curves of $LaMnO_3$, $CaMnO_3$, and $LaGaO_3$ have also been included for comparison [11]. All data shown in Fig. 3 are from insulators having the orthorhimbic (Pbnm) perovskite structure at room temperature. For such a simple structure, a dominant phonon contribution to $\kappa(T)$, which is characterized by the so-called $1/T$ law at sufficiently high temperatures, is expected. Any deviation of $\kappa(T)$ curve from the $1/T$ law can be used as a measurement of the extra scattering in addition to the phonon-phonon scattering.

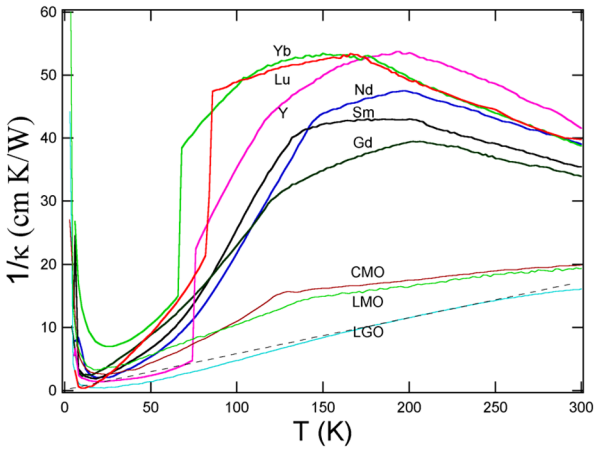

FIG. 3 (color online). Temperature dependence of $1/\kappa(T)$ of RVO_3 perovskites, $LaMnO_3$, $CaMnO_3$, and $LaGaO_3$. The peculiar slope of the $1/\kappa$ vs T curve in the interval $T_N < T < T_\infty$ for $SmVO_3$, $YbVO_3$, and $LuVO_3$ samples has been found to be caused by the sample quality.

The $1/T$ law is only found to describe the $\kappa(T)$ of the diamagnetic insulator $LaGaO_3$. This observation highlights the important role of spin and/or orbital fluctuations. We can further divide the curves of Fig. 3 into two groups by their behavior near room temperature. The magnitudes of the $\kappa(T)$ of $LaMnO_3$ and $CaMnO_3$ are as high as that of $LaGaO_3$ even though the $\kappa(T)$ of the former two deviates from a $1/T$ law because spin-phonon interactions in the paramagnetic phase of these compounds introduce a phonon scattering mechanism on top of the regular phonon-phonon scattering seen in $LaGaO_3$. In contrast, the $\kappa(T)$ of the RVO_3 family at 300 K $> T > T_\infty$ are much lower and their slopes correspond to that of a glass despite the crystalline character of the compounds. How can these highly crystalline compounds show such a remarkable difference in their lattice dynamics? We are forced to conclude that orbital fluctuations in RVO_3 play a role in suppressing phonons. As shown in Fig. 3, T_∞ marks a turning point for the $\kappa(T)$ from a glassy behavior in RVO_3 (R = Nd, ..., Lu, and Y). Since the phonon contribution is partially restored below T_∞, it is apparent that the orbital and spin fluctuations above T_∞ so perturb the periodicity of the V-O bonding that the phonon propagation vector $\mathbf{q}$ is no longer a good quantum number. Considering that the orbital ordering of t electrons is reflected structurally to a less extent than that of e electrons, this observation is significant with regard to the lattice dynamics associated with orbital fluctuations. Thermal conductivity measurements, therefore, provide an alternate probe to orbital ordering.

Orbital ordering in the interval $T_N < T < T_\infty$ partially restores phonon thermal conductivity. Orbital ordering restores some phonon branches as recently observed by infrared spectroscopy [12]. The existence of orbital order raises the possibility that orbitons contribute to $\kappa(T)$ below T_∞. However, a tiny difference between the $\kappa(T)$ below room temperature of $LaMnO_3$ with well-established orbital order and that of $CaMnO_3$ with no orbital degeneracy may imply that thermal energies are not high enough to excite orbitons below room temperature in the $RMnO_3$ perovskites; and a recent Raman study of $RMnO_3$ perovskites confirms this conclusion [13].

A deviation of the $\kappa(T)$ curve from the $1/T$ law in the orbitally ordered paramagnetic state highlights the influence of spin fluctuations on lattice dynamics. In order to demonstrate the influence of spin fluctuations, we have extrapolated to zero the $1/\kappa$ versus T curve in the interval $T_N < T < T_\infty$ for RVO_3 as well as that for $LaMnO_3$ and $CaMnO_3$ above T_N. From Fig. 3, it is obvious that $\kappa(T)$ of the RVO_3 family in the interval $T_N < T < T_\infty$ is closer to the $1/T$ law than that of $LaMnO_3$ and $CaMnO_3$. This observation signals that the spin-phonon interaction is weaker in RVO_3 than in $LaMnO_3$ and $CaMnO_3$, which is consistent with our previous proposal [11] that spin fluctuations modulate the local bond lengths via semicovalent-exchange striction. The M-O-M exchange interaction consists of two terms, i.e., $J \sim T_N \sim [U^{-1} + (2\Delta)^{-1}]$, where U is the on-site correlation energy and Δ is the charge-transfer gap. Mapping of Δ of the semicovalent-exchange component over the transition-metal oxides with perovskite structure shows that Δ is significantly larger for V(III) than for Mn(III) [14]. Therefore, we must consider the possibility that exchange-strictive fluctuations are introducing an added phonon scattering in the interval $T_N < T < T_\infty$ rather than orbitons enhancing $\kappa(T)$. A certain degree of orbital fluctuations may also contribute to the deviation because the spin-orbit coupling forces retention of some orbital fluctuations even below T_∞. The slope change in $\kappa(T)$ at T_N provides clear evidence for a sharp decrease below T_N of the spin-phonon scattering. Moreover, magnons in the magnetically ordered phase may set in to contribute to the steep increase in $\kappa(T)$ on cooling through T_N.

$\kappa(T)$ of $LaVO_3$ and $CeVO_3$ is distinguished from that of the other members of the RVO_3 family by showing a first-order change at a temperature near T_N. The detailed features of $1/\kappa(T)$ and $1/\chi(T)$ for these two compounds are illustrated in Fig. 4 in order to clarify the relationship between T_N and the first-order change of $\kappa(T)$. Unfortunately, the data resolution does not allow us to make a clear assignment of T_N based on the $\kappa(T)$ in $LaVO_3$. Significantly, the $\kappa(T)$ data for both compounds show an additional suppression of the glasslike thermal conductivity in a small temperature interval above T_N with an abrupt restoration of phonons setting in below T_N. This feature is consistent with locally cooperative tetragonal ($c/a < 1$) site distortions above T_N in fluctuating regions of short-range magnetic order as a result of spin-orbit coupling, long-range orbital, and magnetic order below T_N giving the dramatic restoration of phonons.

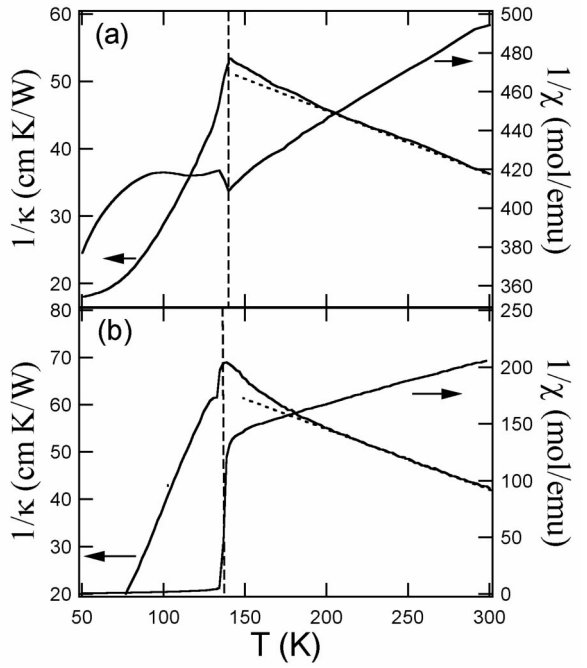

FIG. 4. Temperature dependence of $1/\kappa$ and $1/\chi$ for (a) $LaVO_3$ and (b) $CeVO_3$. $\chi(T)$ was measured at 1 kOe in a zero-field-cooling (ZFC) mode. The dotted lines in the $1/\kappa$ vs T curve above T_N are drawn for clarification.

Moreover, the change from a second-order orbital transition at $T_\infty > T_N$ to a first-order transition at $T_\infty \leq T_N$ can be understood as a change from an orbital order-disorder transition at $T_\infty > T_N$ to an orbital-reorientation transition at $T_\infty \leq T_N$ as occurs at T_{CG} in Fig. 1. In fact, synchrotron diffraction data have suggested an orbital order takes place at $T_N > T_\infty$ in $LaVO_3$ [5]. A nearly identical $\kappa(T)$ behavior in $CeVO_3$ and $LaVO_3$ is clear evidence that a similar sequence of transitions also occurs in $CeVO_3$. However, T_∞ and T_N of $CeVO_3$ appear to be close to each other and are sensitive to the oxygen stoichiometry, which accounts for the controversial results in the literature for this compound [15].

In conclusion, systematic measurements of thermal conductivity and magnetic susceptibility on melt-grown crystals of the RVO_3 perovskites reveal the following: (1) RVO_3 crystals conduct heat like a glass in the orbitally disordered paramagnetic phase due to a strong spin-orbit-lattice coupling. (2) Orbital order in the interval $T_N < T < T_\infty$ allows a partial restoration of the phonons, but a spin-phonon scattering in the paramagnetic phase is at least partially responsible for a $\kappa(T)$ that deviates from the typical phonon thermal conductivity. (3) The suppression of phonon thermal conductivity by orbital fluctuations is particularly strong as $T_N \approx T_\infty$ is approached from above in $LaVO_3$ and $CeVO_3$; this phenomenon is consistent with spin-orbit coupling within regions of short-range antiferromagnetic order. (4) In analogy with the T_{CG} found in RVO_3 (R = Dy, ..., Lu, and Y), a first-order transition of $\kappa(T)$ near T_N suggests that an orbital-reorientation transition takes place at $T \leq T_N$ in $LaVO_3$ and $CeVO_3$. These results, especially the (4) above, make the recent theoretical argument [16] of orbital fluctuations and the type-C magnetic ordering irrelevant in RVO_3. (5) A sharp change of $\kappa(T)$ at T_∞ makes thermal conductivity measurement an alternative method to probe orbital order-disorder transition.

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