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Negative thermal expansion of ReO_3 in the extended temperature range

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We reported previously [T. Chatterji *et al.*, Phys. Rev. B **78**, 134105 (2008)] negative thermal expansion (NTE) in ReO_3 in the limited temperature range from 2 to 220 K. Here we discovered NTE in ReO_3 at higher-temperature region from 600 to 680 K. We determined the temperature variation in the lattice parameter and the unit cell volume of ReO_3 by neutron diffraction. The temperature variation in the lattice parameter and the unit cell volume show two regions of NTE and two minima. We attribute the NTE of ReO_3 to be the result of anharmonicity and anomalous softening of M_3 phonon mode. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3155191]

Negative thermal expansion (NTE), i.e., the decrease in volume or length of a material with increasing temperature is an unusual property exhibited by relatively few materials.[1–5] The phenomenon NTE can arise from a range of different mechanisms, viz., magnetostriction, valence transition, anharmonicity of low energy phonon modes, etc. Here we are concerned with the anharmonicity of low energy phonon modes, which is believed to be the origin of the NTE in oxide-based framework materials.[1,6–10] The NTE materials have generated significant scientific and commercial interest because they can be used to compensate the more usual positive thermal expansion (PTE) of usual materials. In recent years intense investigations of materials scientists have led to the discovery of several new materials[11–13] that show NTE behavior.

Transition metal oxides have been the subject of renewed interest ever since high temperature superconductivity was discovered in copper oxide materials. The transition metal oxides with narrow *d* bands form strongly correlated Mott–Hubbard systems, in which conventional band theory is no longer valid.[14] The number of transition metal oxides where band theory alone can provide adequate account of their properties is quite limited, and is confined to compounds of the 4*d* and 5*d* series. ReO_3 is an example of such a simple metallic oxide. Among *d*-electron conductors, ReO_3 has a simple perovskitelike cubic structure and its conductivity is comparable to that of Ag. Although the electron-phonon coupling constant is not very small[15] (the coupling constant $\lambda=0.34$), ReO_3 surprisingly does not show superconductivity down to 20 mK. ReO_3 seems to belong to the normal class of conventional band Fermi liquids with electron-phonon interactions dominating the resistivity.[15] ReO_3 crystallizes in the cubic space group ($Pm3m$) with the undistorted perovskitelike DO_9 type structure with lattice constant $a=3.74$ Å. The structure consists of corner-linked ReO_6 octahedra with Re at the centers and linear Re–O–Re links. Among the numerous perovskitelike compounds, ReO_3 belongs to a small family of undistorted cubic structures, which is stable at ambient pressure and at all temperatures up to its melting point. Also, the ReO_3 structure has a completely vacant *A* cation site of the ABO_3 perovskite structure. This empty structure is therefore expected to allow rigid rotation of the ReO_6 octahedra. The cubic perovskite structure in ReO_3 is essentially unstable due to the softening of the M_3 phonon mode involving rigid rotation of the ReO_6 octahedra. Although the average crystal structure appears cubic, the real nanoscale local structure may be more complex. The rigid unit modes involved in the structural instability should lead to NTE.[1] We therefore investigated the temperature dependence of the lattice parameter of ReO_3 by neutron diffraction. We reported[16] NTE in ReO_3 in the limited temperature range from 2 to 220 K. Similar results have been reported by other groups of researchers.[17–19] Here we report temperature variation in the lattice parameter in ReO_3 in an extended temperature range from 2 K to 800 K measured by neutron powder diffraction. We discovered that ReO_3 also shows NTE region (600–680 K) at higher temperatures.

Neutron diffraction measurements on ReO_3 powders were done on diffractometer D20 (Ref. 20) at the Institut Laue-Langevin in Grenoble. The dry polycrystalline sample was put inside a vanadium can and was sealed, and was placed inside a He cryofurnace that can generate temperature in the range from about 2 to 550 K during the first part of the experiment. In the second part of the experiment, we put the dry sample inside the vanadium can that was kept in vacuum inside a high temperature furnace that could generate temperature up to about 1300 K. The diffraction intensities from ReO_3 were measured in the temperature range of 2–800 K by using the above mentioned sample environment devices. The neutron wavelength was determined to be $\lambda=1.359\pm0.001$ Å from the wavelength calibration measurement with NIST Si640b as a standard.

Figure 1 shows a typical diffraction diagram of ReO_3 measured at $T=2-4$ K along with the results of the Rietveld profile fit. The Re and O atoms in ReO_3 structure ($Pm3m$) occupy special positions $\left[\mathrm{Re}:(1a)000;\mathrm{O}:(3d)\frac{1}{2}00\right]$ and have no positional fit parameters in the cubic $Pm3m$ phase. So only the lattice parameter, the thermal displacement parameters of Re and O atoms, and the scale factor were refined. The agreement factor *R* was about 2%. Figure 2 shows the

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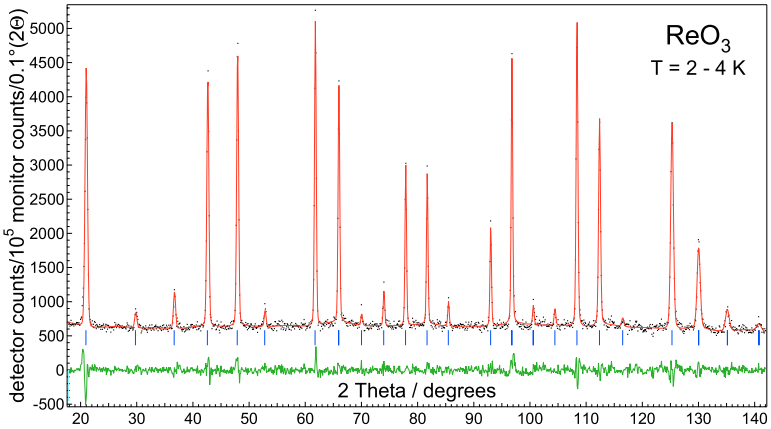

FIG. 1. (Color online) Diffraction intensity of ReO_3 measured at $T=2-4$ K using neutron wavelength $\lambda=1.359$ Å on the diffractometer D20 of the Institut Laue-Langevin along with the results of Rietveld refinement.

temperature variation in the cubic lattice parameter a and the unit cell volume V. The lattice parameter and the unit cell volume decreases continuously as the temperature is increased from $T=2$ to about $T=220$ K, and exhibits a minimum at about this temperature. At higher temperatures, they first increase with increasing temperature in a normal way up to about 600 K. They decrease again and show a second minimum at about $T=680$ K and increase at higher temperatures in a normal way up to about 800 K, the maximum temperature investigated during the present experiment. The total volume contraction from 2 to 220 K is about 0.036% and is rather small, but is much larger than the experimental error. The volume contraction at second NTE range 600–680 K is even smaller but is much larger than the experimental error bars. Also, the temperature variation in the lattice parameter and the unit cell volume show a "V"-shape minimum at about 680 K that is different from the "U"-shape minimum observed at about 220 K.

The point group symmetries of the special positions occupied by Re ($1a$) and O ($3d$) atoms allow only isotropic thermal displacement parameters for Re, while O atoms can have anisotropic thermal displacement parameters with two components $\beta 11=\beta_{\parallel}$ and $\beta 22=\beta 33=\beta_{\perp}$, which represent vibrations parallel and perpendicular to the Re–O bond, respectively. The isotropic thermal parameter of Re is rather small and behaves in a normal way and therefore is not shown. The temperature variation in thermal displacement parameters of oxygen atoms is shown in Fig. 3. The $\beta 11=\beta_{\parallel}$ of O is small and is almost temperature independent, whereas the $\beta 22=\beta 33=\beta_{\perp}$ of the O atom is much larger and increases strongly with temperature. Thus the O atoms in ReO_3 have highly anisotropic thermal vibrations. The large thermal vibration amplitude $\beta_{\perp}$ perpendicular to the Re–O bond direction is consistent with the soft M_3 phonon mode. The thermal displacemater obtained by us compare well with the previously reported values[21] measured at $T=300$ K up to a much larger value of Q also on a powder ReO_3 sample but at a spallation neutron source. The temperature dependence of the thermal displacement parameters also agrees very well with that measured by single crystal x-ray diffraction.[22] The temperature variation in thermal displacement parameters obtained in two different sets of experiments with different sample environments (cryofurnace and high temperature furnace) do not match exactly with each other and therefore there are abrupt changes in the temperature variation in the thermal displacement parameters given in Fig. 3. However these mismatches are hardly significant and are within experimental accuracy and therefore can be neglected.

The origin of second region of NTE is not yet understood. We speculate that it is related to a probable anomalous temperature dependence of the M_3 phonon mode at this tem-

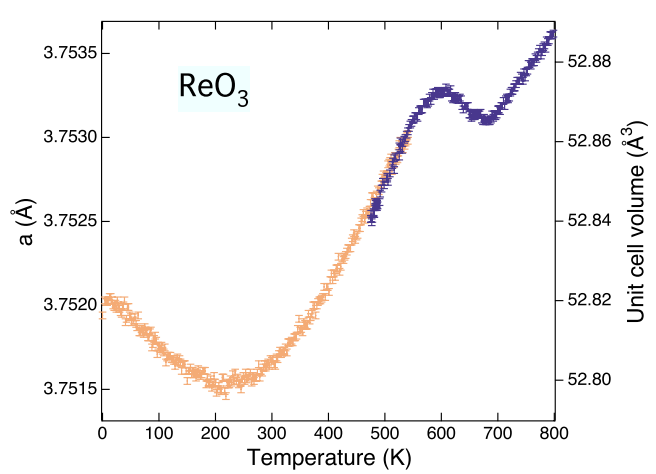

FIG. 2. (Color online) Temperature variation in the lattice parameter a and the unit cell volume V of ReO_3. The measurements were done with two different setups shown in two different colors.

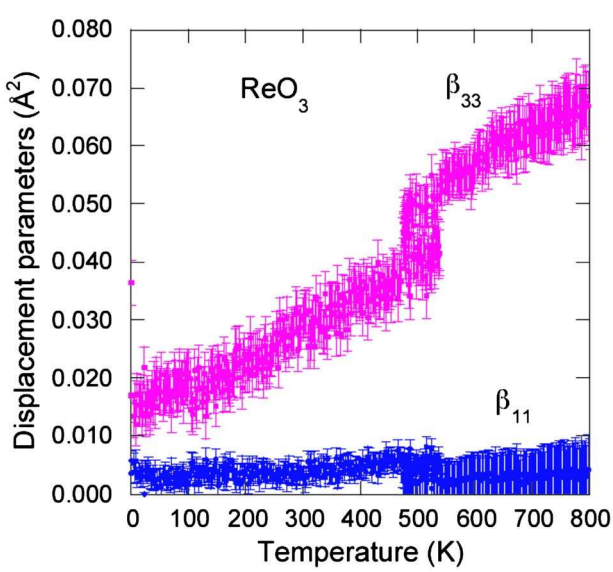

FIG. 3. (Color online) Temperature variation in the thermal displacement parameters of O atoms of ReO_3. Small steps in the temperature variation seen in this figure due to the mismatch between the data measured with two different experimental setups are within error and can be neglected.

perature range. We reproduced qualitatively from our lattice dynamical calculations[16] the NTE behavior of ReO_3 in the temperature range of 2–220 K. We ascribed the NTE at low temperature to the negative Grüneisen parameter of the zone boundary M_3 phonon mode representing the antiphase rotations of the neighboring ReO_6 octahedra. Also, we recently reported[23] the softening of the M_3 phonon at low temperature by measuring the temperature of this phonon mode in the range of 2–300 K. Unfortunately, not knowing the second high temperature lattice anomaly in ReO_3, we did not measure the temperature dependence of the M_3 phonon frequency at high temperatures.

We have done powder neutron diffraction investigation of the temperature variation in the average structure of ReO_3 in the extended temperature range of 2–800 K. We measured neutron diffraction intensities with very fine temperature steps and have determined the temperature variation in the lattice parameter and the unit cell volume of ReO_3 and have found NTE in the low temperature range of 2–220 K. Above about 220 K the thermal expansion becomes positive and remains so up to about 600 K. We discovered a further NTE behavior with a second local minimum volume at about 680 K. We ascribe the NTE of ReO_3 at low temperatures to the negative Grüneisen parameter of the zone boundary M_3 phonon mode representing the antiphase rotation of the neighboring ReO_6 octahedra. The origin of the second NTE range is not yet understood but may possibly be related to anomalous behavior of the M_3 phonon mode.

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