Pressure-induced structural phase transitions and phonon anomalies in ReO$_3$:
Raman and first-principles study

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We report high-pressure Raman-scattering studies on single-crystal ReO$_3$ up to 26.9 GPa at room temperature, complemented by first-principles density functional calculations to assign the modes and to develop understanding of the subtle features of the low-pressure phase transition. The pressure (P) dependence of phonon frequencies (ω) reveals three phase transitions at 0.6, 3, and 12.5 GPa with characteristic splitting and changes in the slope of $\omega(P)$. Our first-principles theoretical analysis confirms the role of the rotational modes of ReO$_6$, M_3, to the lowest pressure structural transition, and shows that the transition from the $Pm3m$ to the $Im3$ structure is a weak first-order transition, originating from the strong anharmonic coupling of the M_3 modes with the acoustic modes (strain).

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I. INTRODUCTION

ABO$_3$ perovskite oxides exhibit a diverse range of phenomena ranging from magnetoresistance, superconductivity to ferroelectricity [1]. Typically, the insulating perovskite oxides, such as BaTiO$_3$, are known to commonly exhibit temperature- (T-) induced structural phase transitions in which the vanishing occupation of d orbitals of a transition-metal ion at the B site is a key to its off-centering as well as to the symmetry lowering structural instability. In contrast, T-dependent structural transitions are not common in metallic perovskite oxides, which typically have the d orbitals of their transition metal partially occupied by electrons. Competing structural instabilities in a perovskite involve rotations of the BO$_6$ octahedra, which are not excluded by the partial occupancy of d orbitals of the B cation [2]. When the size of the B cation relative to that of the A cation is large, the cubic perovskite structure can be unstable with respect to such octahedral rotational modes, and this can be another factor that can lead to structural transitions [1] and be used to understand fundamentally interesting structural transitions in metallic perovskite oxides. From this angle, ReO$_3$ is a rather interesting metallic perovskite oxide having conductivity within a factor of 6 of that of copper at room temperature and ∼100% reflectivity below the plasma edge at 2.1 eV. Here, the A cation is completely missing, and four pressure-dependent (but interestingly no temperature-dependent) structural transitions are observed.

At ambient pressure, the structure of ReO$_3$ is cubic (space group $Pm3m$) consisting of corner-linked ReO$_6$ octahedra and linear Re-O-Re bonds. The empty A cation site in ReO$_3$ promotes structural instabilities involving rotations of the rigid ReO$_6$ octahedra. The early interest in ReO$_3$ was triggered by an observation of a supposedly continuous phase transition

at ∼0.5 GPa at room temperature with the compressibility being an order of magnitude higher in the high-pressure phase [3] (and hence termed as "compressibility collapse transition"). Early neutron-diffraction measurements showed that the high-pressure phase is tetragonal ($P4/mbm$), which transforms at a slightly higher pressure of 0.72 GPa to the cubic II ($Im3$) phase [4]. However, recent neutron-diffraction studies do not find any evidence of the tetragonal ($P4/mbm$) intermediate phase between the two cubic structures [5]. The softening of the M_3 phonon mode was suggested to be the driving force behind the $Pm3m$ to $Im3$ pressure transition. X-ray diffraction at high pressures by Jorgensen *et al.* [6] showed three other phase transitions; a cubic II ($Im3$) phase to a monoclinic MnF$_3$ related phase at 3 GPa to the rhombohedral VF$_3$ related phase (rhombohedral I) at 12 GPa and to another rhombohedral phase (rhombohedral II) at 38 GPa. Subsequent high-pressure x-ray diffraction studies by Suzuki *et al.* [7] did not observe the monoclinic phase and showed that the cubic phase and rhombohedral I phase coexist in the pressure range of 8–18 GPa. Biswas *et al.* [8] have recently reported pressure-induced phase transitions in nanocrystalline ReO$_3$ using synchrotron x-ray diffraction. They have shown that the ambient pressure cubic I phase ($Pm3m$) changes to the monoclinic phase ($C2/c$) at ∼0.3 GPa and from the monoclinic to a rhombohedral I phase ($R3c$) at ∼6.7 GPa and finally to a rhombohedral II phase at ∼20.3 GPa.

Purans *et al.* [9] have carried out Raman measurements at room temperature and ambient pressure. We carry out a high-pressure Raman study of crystalline ReO$_3$ here. We have carried out high-pressure Raman measurements up to 26.9 GPa on single crystals of ReO$_3$ showing three phase transitions at 0.6, 3, and 12.5 GPa. The pressure derivatives of the phonon frequencies have been determined. Our results for the high-pressure transitions corroborate the x-ray diffraction results of Jorgensen *et al.* [4]. However, the low-pressure structural transition at $P \sim 0.6$ GPa is quite intriguing, and we

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