Zone center phonons of the orthorhombic RMnO$_3$ (R = Pr, Eu, Tb, Dy, Ho) perovskites
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Abstract
A short range force constant model (SRFCM) has been applied for the first time to investigate the phonons in RMnO$_3$ (R = Pr, Eu, Tb, Dy, Ho) perovskites in their orthorhombic phase. The calculations with 17 stretching and bending force constants provide good agreement for the observed Raman frequencies. The infrared frequencies have been assigned for the first time.

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Introduction
Until recently the RMnO$_3$ perovskites (R = rare earth elements) have been the object of research mainly as parent materials of mixed valence manganites exhibiting colossal magnetoresistivity (CMR) [1-4]. In the past few years, however, there is an increased interest in the complex relationships among the lattice distortions, magnetism, dielectric, and transport properties of undoped RMnO$_3$ [5-10]. All RMnO$_3$ perovskites show a distortion of MnO$_6$ octahedra due to orbital ordering characteristic of the John-Teller effect of Mn$^{3+}$ cations [11-15]. An investigation of infrared and Raman frequencies will be quite useful in describing the details of such properties. Practically, very limited information is available on the infrared and Raman scattering of orthorhombic RMnO$_3$. Martin Carron et al. [11] studied the behavior of Raman phonons through the transition from static to dynamic Jahn-Teller order in stoichiometric RMnO$_3$ samples (R = La, Pr, Y). Also Martin Carron et al. [12] studied orthorhombic RMnO$_3$ (R = Pr, Nd, Eu, Tb, Dy, Ho) manganites for their Raman phonons as a function of the rare earth ions and temperature. They had assigned only some of the Raman modes. They correlated the frequencies of three most intense modes of orthorhombic samples, with some structural parameters such as Mn-O...
bond distances, octahedral tilt angle and Jahn-Teller distortion. Further rationalization of the Raman spectra of orthorhombic RMnO$_3$ (R = Pr, Nd, Tb, Ho, Er) and different phases of Ca- or Sr-doped RMnO$_3$ compounds as well as cation deficient RMnO$_3$ were made by Martin Carron et al. [13]. Their assignment of the peaks related to octahedral tilt were in good agreement with the other authors but the assignment of peak to an antisymmetric stretching associated with the Jahn-Teller distortion was doubtful. Wang Wei-Ran et al. [14] measured Raman active phonons in orthorhombic RMnO$_3$ (R = La, Pr, Nd, Sm) compounds and they also assigned three main Raman peaks. Recently, the polarized Raman spectra of orthorhombic RMnO$_3$ (R = Pr, Nd, Eu, Gd, Tb, Dy, Ho) series at room temperature were studied by Iliev et al. [15] where they had assigned the observed frequencies to nine Raman modes. Their study shows that the variations of lattice distortions with radius of rare earth atoms affect significantly both the phonon frequencies and the shape of some of Raman modes. To our knowledge, the theoretical investigations of phonons, using the normal coordinate analysis in the orthorhombic NdMnO$_3$ has first been made by Gupta et al. [16].

In the present study, the theoretical investigations of phonons in the orthorhombic RMnO$_3$ have been made using the normal coordinate analysis. It has been observed that a total of 17 inter-atomic force constants, which include 8 bending force constants, are enough to obtain a good agreement between theory and experiment for the Raman frequencies. The assignments of infrared frequencies along with their corresponding eigen vectors observing the atomic displacements in the respective vectors have been made for the first time. There is always some scope of more precise infrared experiments to verify these theoretical values.

**Theory**

The structure of stoichiometric RMnO$_3$ shown in Fig. 1, described at room temperature by the Pbnm space group (Z = 4), can be considered as orthorhombically distorted superstructure of ideal perovskites. In the Pbnm structure the atoms occupy four non equivalent atomic sites of them only the Mn site is a center of symmetry [17]. The distortion of the orthorhombic perovskites characterized by the tilting angle of the MnO$_6$ octahedra progressively increases from Pr to Er due to simple steric factors. Additionally, all of the perovskites show a distortion of the MnO$_6$octahedra due to orbital ordering characteristic of the Jahn-Teller of the Mn$^{3+}$ cations. Structural data of EuMnO$_3$ is very recent because of its high neutron absorption and they are perfectly correlated with the other members of RMnO$_3$ series [18].

The total number of irreducible representations for RMnO$_3$ are

$$= 7A_g + 7B_{1g} + 5B_{2g} + 5B_{3g} + 8A_u + 8B_{1u} + 10B_{2u} + 10B_{3u}$$
There are four Raman active species, $A_{g}$, $B_{1g}$, $B_{2g}$ and $B_{2g}$, three infrared active species $B_{1u}$, $B_{2u}$ and $B_{3u}$ and inactive species $A_{u}$.

In the present paper, an attempt has been made to study the zone center phonons in $\text{RMnO}_3$ ($R = \text{Pr, Eu, Tb, Dy, Ho}$) for the first time using SRFCM. We have used nine valence force constants $K_1(\text{Mn-O2})$, $K_2(\text{Mn-O1})$, $K_3(\text{Mn-O2})$, $K_4(\text{R-O1})$, $K_5(\text{R-O2})$, $K_6(\text{R-O1})$, $K_7(\text{R-O2})$, $K_8(\text{R-O1})$, $K_9(\text{R-O2})$; and eight bending force constants $H_1(\text{O1-R-O1})$, $H_2(\text{O1-R-O1})$, $H_3(\text{O1-R-O1})$, $H_4(\text{O1-R-O2})$, $H_5(\text{O1-R-O2})$, $H_6(\text{O2-R-O2})$, $H_7(\text{O2-R-O2})$ and $H_8(\text{O2-R-O2})$ at various inter-atomic distances and angles as shown in Table 1 (only for PrMnO$_3$).

![Figure 1](image)

**Figure 1**
The structure of Orthorhombic R$\text{MnO}_3$ ($R = \text{Pr, Nd, Eu, Gd, Tb, Dy, Ho}$) compounds at room temperature, belonging to Pbnm space group. The structure has four formulae unit with R atoms, Mn atoms and O atoms (O1 and O2).

Table 1: Force constant, Coordination number, Inter-atomic Distances (Å) and Angles (deg) and Force constant values (N/cm) for Orthorhombic Pr$\text{MnO}_3$

| Force constant | $K_1$ | $K_2$ | $K_3$ | $K_4$ | $K_5$ | $K_6$ | $K_7$ | $K_8$ | $K_9$ | $H_1$ | $H_2$ | $H_3$ | $H_4$ | $H_5$ | $H_6$ | $H_7$ | $H_8$ |
|----------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| Coord. Number. Distance/ Angle | 8 | 8 | 8 | 4 | 8 | 4 | 8 | 4 | 8 | 8 | 8 | 8 | 8 | 4 | 4 | 8 | 8 | 7 | 8 |
| Force constant values | 1.91 | 1.95 | 2.21 | 2.36 | 2.40 | 2.48 | 2.62 | 3.17 | 3.52 | 89 | 67 | 110 | 90 | 56 | 66 | 160 | 120 |

| Force constant | $K_1$ | $K_2$ | $K_3$ | $K_4$ | $K_5$ | $K_6$ | $K_7$ | $K_8$ | $K_9$ | $H_1$ | $H_2$ | $H_3$ | $H_4$ | $H_5$ | $H_6$ | $H_7$ | $H_8$ |
|----------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| Coord. Number. Distance/ Angle | 0.597 | 0.535 | 0.950 | 0.456 | 0.019 | 0.311 | 0.382 | 0.335 | 0.598 | 0.432 | 0.413 | 0.404 | 0.373 | 0.338 | 0.329 | 0.136 | 0.022 |
Results and Discussions

A systematic variation in the most of the force constants is seen throughout the series. It was interesting to observe that although, the interatomic distances for K1 and K3 between Mn and O2 atoms remain nearly unchanged from Pr to Ho but the force constant exhibited a uniform increase. This behaviour can be related to the increase in distortion of MnO6 octahedra. Further, as shown in Table 1 the force constant K3 (0.950 N/cm) is quite large when compared with the similar force constant obtained in studies of NdNiO3 [19] and NdGaO3 [20] (0.620 N/cm). A similar kind of behaviour of large force constant between Mn and O2 atoms was observed in pyrochlore manganates [21]. This may be one of the possible reasons of associated CMR properties of manganese compounds. To account for a drastic change in resistivity and a low critical temperature in such materials, it should be noted that the double exchange model must be combined with the effect of the Jahn-Teller distortion of MnO6 octahedra [22]. This effect promotes carrier localization and dresses charge carriers via cloud of phonons. It is in this respect where the large interatomic force between Mn and O2 atoms plays an important role, being a part of the distortion of the MnO6 octahedra. The force constants between R and O1 atoms, K4 and K6 increase with decrease of R-O1 distance almost uniformly throughout the series. The force constant K8 (R-O1) changes by a small amount as the R-O1 distance also shows the similar behavior. The force constants K5, K7 and K9 also show a uniform increase. Although force constant K5 is very

| Modes | *Pr | Pr | *Eu | Eu | *Tb | Tb | *Dy | Dy | *Ho | Ho |
|-------|-----|----|-----|----|-----|----|-----|----|-----|----|
| A<sub>g</sub> | 491 | 491 | 501 | 501 | 509 | 509 | 513 | 513 | 520 | 520 |
| B<sub>1g</sub> | 607 | 607 | 610 | 610 | 612 | 612 | 614 | 614 | 615 | 615 |
| B<sub>2g</sub> | 627 | 611 | 621 | 621 | 624 | 624 | 617 | 617 |
| B<sub>3g</sub> | 400 | 429 | 432 | 432 | 432 | 432 | 454 | 454 |

Table 2: *Observed [15] and Calculated Raman Wave Numbers (cm<sup>-1</sup>) for Orthorhombic RMnO<sub>3</sub> (R = Pr, Eu, Tb, Dy, Ho)
small but K9 shows comparatively a large value. The bending force constants H1-H4 show a very small change in force constant values while H7 and H8 exhibit uniformly increasing values.

The calculated Raman frequencies in Table 2 agreed satisfactorily with the observed values [15]. The assignment of infrared frequencies as shown in Table 3 has been done for the first time. Still a precise experimental analysis of infrared frequencies is needed to verify the results of present calculations. The potential energy distribution (PED) for most of the force constant is found to be almost similar throughout the series. The PED showed that high wave numbers are dominated by stretching force constants involving Mn and O atoms and bending force constants having R and O atoms. Therefore, the symmetric stretching of the basal oxygens of the octahedra, around 610 cm⁻¹ (B1g symmetry); the asymmetric stretching at about 490 cm⁻¹ (A₅ symmetry) associated with the Jahn-Teller distortion is expected. The A₅ mode (324 cm⁻¹- 395 cm⁻¹) showing a drastic increase in frequency is purely a stretching mode dominated by K9 (R-O2). Most of the lower wave number modes have a convincing influence by R-O bending and stretching force constants. For all the compounds of the orthorhombic RMnO₃ series, we calculated the eigen vectors

| Modes | Pr | Eu | Tb | Dy | Ho |
|-------|----|----|----|----|----|
| B1u   | 608| 611| 612| 614| 617|
|       | 569| 581| 581| 580| 582|
|       | 485| 492| 509| 514| 516|
|       | 303| 323| 328| 332| 338|
|       | 205| 213| 214| 214| 223|
|       | 141| 152| 158| 159| 161|
|       | 133| 135| 142| 144| 143|
|       | 0  | 0  | 0  | 0  | 0  |
| B2u   | 614| 612| 617| 620| 620|
|       | 571| 582| 582| 580| 580|
|       | 467| 494| 498| 500| 511|
|       | 389| 395| 406| 417| 410|
|       | 290| 304| 309| 312| 318|
|       | 223| 229| 232| 234| 235|
|       | 201| 206| 208| 208| 213|
|       | 177| 176| 180| 179| 178|
|       | 132| 142| 148| 148| 149|
|       | 0  | 0  | 0  | 0  | 0  |
| B3u   | 535| 538| 551| 558| 562|
|       | 484| 505| 515| 519| 522|
|       | 431| 458| 463| 465| 474|
|       | 343| 384| 398| 406| 419|
|       | 315| 320| 318| 316| 315|
|       | 244| 268| 272| 277| 289|
|       | 181| 181| 185| 184| 184|
|       | 131| 137| 143| 144| 143|
|       | 106| 115| 118| 120| 122|
|       | 0  | 0  | 0  | 0  | 0  |
representing the displacements of various atoms. It was observed that for larger wave numbers, the displacement of O atoms is important whereas for smaller wave numbers, the displacement of R atoms dominates as given in Table 4 and Table 5 only for PrMnO₃. Vibrations of several atoms are involved in some middle order modes.
Table 5: Calculated Infrared Wave Numbers (cm⁻¹) of PrMnO₃ along with their Eigen-vector Lengths representing Atomic Displacements for various Atoms

| Modes | Wave-numbers | Mn   | Mn   | Mn   | Pr   | Pr   | O1   | O1   | O2   | O2   |
|-------|--------------|------|------|------|------|------|------|------|------|------|
| B1u   | 606          | -0.02| -0.02| 0.01 | -0.10| 0.95 | 0.11 | -0.06| 0.25 |
|       | 569          | 0.02 | -0.53| 0.03 | 0.01 | -0.10| 0.84 | -0.04| -0.02|
|       | 485          | 0.08 | -0.05| -0.27| -0.07| 0.09 | 0.03 | 0.94 | -0.16|
|       | 303          | -0.19| 0.01 | -0.17| -0.35| -0.26| 0.02 | 0.12 | 0.86 |
|       | 205          | 0.95 | 0.01 | 0.20 | -0.20| -0.05| -0.01| 0.00 | 0.15 |
|       | 141          | -0.24| -0.25| 0.76 | -0.48| -0.01| -0.17| 0.17 | -0.12|
|       | 133          | -0.07| 0.81 | 0.23 | -0.14| -0.04| 0.50 | 0.08 | -0.07|
|       | 0            | 0.00 | 0.00 | 0.47 | 0.76 | 0.00 | 0.00 | 0.26 | 0.36|
| B2u   | 614          | -0.01| -0.03| 0.00 | 0.07 | 0.04 | 0.02 | 0.93 | -0.25| 0.14 |
|       | 571          | 0.02 | -0.53| 0.02 | 0.06 | -0.06| 0.00 | -0.14| -0.01| 0.83 |
|       | 467          | -0.01| -0.01| -0.03| -0.30| -0.22| 0.21 | 0.88 | 0.03 | 0.18 |
|       | 389          | -0.04| 0.00 | 0.10 | -0.04| -0.07| 0.96 | 0.01 | 0.19 | 0.01 |
|       | 290          | -0.27| 0.01 | -0.08| -0.10| 0.03 | -0.08| -0.24| -0.15| 0.02 |
|       | 223          | -0.14| 0.42 | 0.00 | 0.81 | -0.32| 0.01 | -0.08| 0.06 | 0.17 |
|       | 201          | 0.93 | 0.10 | 0.19 | 0.06 | -0.06| -0.01| -0.07| -0.05| 0.03 |
|       | 177          | -0.20| 0.04 | 0.97 | -0.07| -0.03| -0.12| 0.00 | 0.01 | 0.01 |
|       | 132          | -0.02| 0.56 | -0.08| -0.56| -0.46| -0.01| 0.17 | 0.35 | -0.10|
|       | 0            | 0.00 | 0.47 | 0.00 | 0.00 | 0.76 | 0.00 | 0.26 | 0.36 | 0.00 |
| B3u   | 535          | -0.25| 0.07 | -0.04| -0.21| -0.07| 0.27 | 0.59 | -0.49| 0.46 |
|       | 484          | 0.15 | -0.05| 0.10 | -0.28| 0.03 | 0.85 | -0.21| -0.10| 0.33 |
|       | 431          | -0.21| 0.10 | -0.04| -0.04| 0.19 | 0.30 | 0.16 | 0.81 | 0.35 |
|       | 343          | -0.04| -0.53| 0.02 | -0.30| 0.22 | -0.14| 0.57 | 0.15 | -0.45|
|       | 315          | 0.05 | 0.82 | -0.02| -0.12| 0.13 | -0.09| 0.25 | 0.01 | -0.31|
|       | 244          | -0.25| -0.14| -0.01| 0.21 | -0.19| 0.07 | -0.16| -0.05| 0.24 |
|       | 181          | -0.26| 0.03 | 0.95 | 0.14 | 0.05 | 0.03 | 0.06 | 0.00 | -0.07|
|       | 131          | -0.06| -0.03| -0.06| 0.12 | 0.93 | 0.00 | -0.19| -0.24| 0.15 |
|       | 106          | 0.71 | -0.06| 0.29 | -0.40| 0.05 | -0.15| 0.02 | 0.06 | 0.41 |
|       | 0            | 0.47 | 0.00 | 0.00 | 0.76 | 0.00 | 0.26 | 0.36 | 0.00 | 0.00 |

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