

# Rattling phonon modes in quadruple perovskites

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Anharmonic vibrations of weakly bound ions in an oversized atomic cage formed by the other atoms are commonly known as rattling. They have been observed in materials such as  $\text{VA}_{10+\delta}$  [1], clathrates [2], dodecaborides [3], filled skutterudites [4],  $\beta$ -pyrochlore oxides [5]. Rattling or other types of anharmonicity can lead, e.g., to Schottky-type anomaly of specific heat at low temperature [6], result in significant increase of electron effective mass [7–9], suppress thermal conductivity [10, 11] or be a driving force for the superconductivity [7–9, 12].

Recently, the rattling has been suggested for quadruple perovskite  $\text{CuCu}_3\text{V}_4\text{O}_{12}$  synthesized under a high-pressure [13]. In quadruple perovskites  $\text{AA}'_3\text{B}_4\text{O}_{12}$  the  $A$  site ions are icosahedrally (twelve neighbors) coordinated by oxygen atoms. The thermal displacement parameter of Cu ions at  $A$  site in  $\text{CuCu}_3\text{V}_4\text{O}_{12}$  was found to be quite large,  $U_{\text{iso}} \approx 0.045 \text{ \AA}^2$  at 300 K. Together with unusual behavior of specific heat  $C_p(T)$  this led to suggestion of possible rattling in  $\text{CuCu}_3\text{V}_4\text{O}_{12}$  [13].

In the present paper we report direct evidence of a rattling mode in  $\text{CuCu}_3\text{V}_4\text{O}_{12}$  and another recently synthesized quadruple perovskite  $\text{CuCu}_3\text{Fe}_2\text{Re}_2\text{O}_{12}$ . The total energy density functional theory (DFT) calculations clearly show rattling distortions along [111] direction related to the Cu vibration.

The electronic structure calculations were performed in the local density approximation taking into account Coulomb repulsion within LDA +  $U$  method [14] using the Vienna *ab initio* simulation package (VASP) [15]. The experimental crystal structure data with the space groups  $Im\bar{3}$  (# 204) and  $Pn\bar{3}$  (# 201) reported in [13] and [16] for  $\text{CuCu}_3\text{V}_4\text{O}_{12}$  and  $\text{CuCu}_3\text{Fe}_2\text{Re}_2\text{O}_{12}$ , respectively, were used.

The crystal structure of quadruple perovskites  $\text{AA}'_3\text{B}_4\text{O}_{12}$  on example of  $\text{CuCu}_3\text{Fe}_2\text{Re}_2\text{O}_{12}$  is shown in Fig. 1a.  $\text{CuCu}_3\text{V}_4\text{O}_{12}$  has a similar structure with V ions occupying both octahedral positions. Crystallographically, there are two different Cu positions. Our calculations, as well as previous results [17] show that Cu at  $A$  sites (i.e. those, which are in icosahedra) have  $3d^{10}$  electronic configuration, i.e., these are  $\text{Cu}^{1+}$  ions. Cu ions at  $A'$  site have local magnetic moment and these are Jahn–Teller active  $\text{Cu}^{2+}$  ions.

In  $\text{CuCu}_3\text{V}_4\text{O}_{12}$  distance between  $\text{Cu}^{1+}$  and surrounding oxygen ions (2.548 Å) is much larger than the sum of corresponding ionic radii 2.13 Å [18]. This is the reason why there develops a localized phonon mode with Cu vibrating in this large  $\text{O}_{12}$  cage, a rattling mode. The dependence of DFT +  $U$  total energy on  $\text{Cu}^{1+}$  displacement has a minimum at  $\sim 0.35 \text{ \AA}$  distortion. Thus our calculations directly demonstrate presence of the rattling mode in  $\text{CuCu}_3\text{V}_4\text{O}_{12}$ . Moreover, this mode does not seem to be specific for this particular material, and therefore we tested whether rattling vibrations are present in another quadruple perovskite, namely, recently synthesized  $\text{CuCu}_3\text{Fe}_2\text{Re}_2\text{O}_{12}$  [16].

There are several possible types of rattling. Indeed, as one can see from Fig. 1a there are two Cu1 ions in the unit cell: those sitting in the center of cube and in its corners. Therefore, rattling distortions of these two Cu1 ions can be in the same [111] direction (in-phase distortion), or in the opposite directions when we have two different Cu1–Cu1 distances (out-of-phase distortions). Moreover, there are two inequivalent by symmetry out-of-phase distortions with Cu1 ions moving to Fe or Re ions between them. Fig. 1b summarizes results of calculations for these 3 types of possible rattling distortions. One can see that this is the out-of-phase distortion to Fe ions, which gives the lowest total energy.

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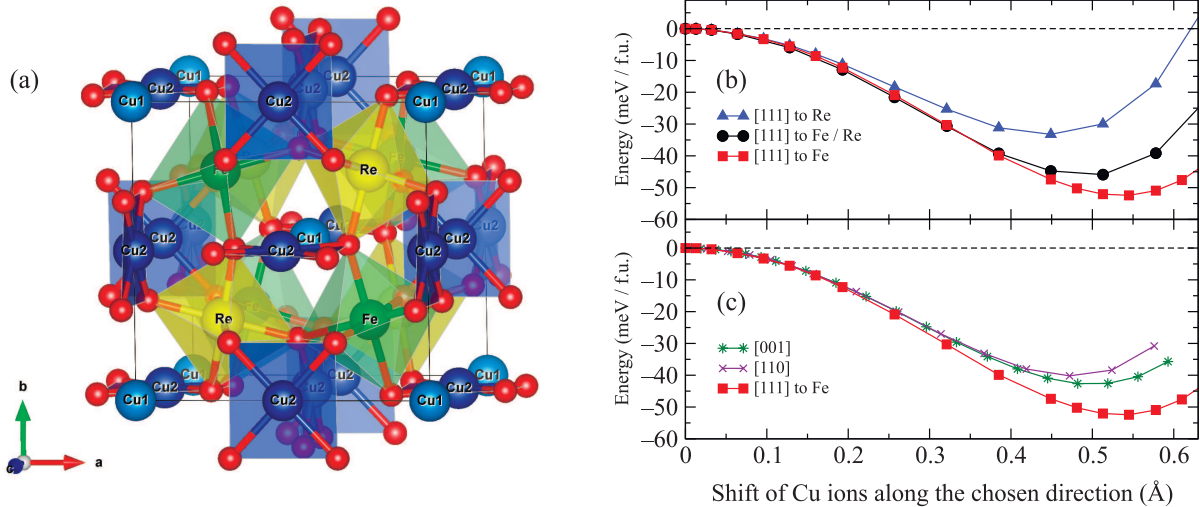


Fig. 1. (Color online) (a) – Crystal structure of quadruple perovskites  $AA'_3B_4O_{12}$  on example of  $CuCu_3Fe_2Re_2O_{12}$ . There are two types of Cu ions: Cu1 (light blue) is in a large cage,  $A$  site, and can rattle, while Cu2 (dark blue) is in square-planer coordinated  $A'$  site.  $FeO_6$  and  $ReO_6$  octahedra are shown by yellow and green, respectively. In  $CuCu_3V_4O_{12}$ , both these octahedra are filled by V ions instead of Fe and Re. (b) – Total energy vs Cu1 displacement along [111] direction, when two different Cu1 ions in a unit cell are shifted both to Re, one to Re and one to Fe, and both to Fe atoms, and (c) along [001], [110], and [111] directions in  $CuCu_3Fe_2Re_2O_{12}$

We checked other directions of possible rattling distortions and found that there are indeed local minima in [001], along [110] directions, but all of them have higher energies than the one along [111] direction, see Fig. 1c. This result demonstrates that the potential for the rattling has a complex form with many local minima and can not be described by a simplified double-well shape.

In conclusion, we provide theoretical evidence of the presence of rattling modes in quadruple perovskite  $CuCu_3V_4O_{12}$ . We predict the same phenomenon in the recently synthesized  $CuCu_3Fe_2Re_2O_{12}$ . The [111] direction of Cu1 rattling turns out to be the most energetically favourable.

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