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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 $VAl_{10+\delta}$ [1], clathrates [2], dodecaborides [3], filled skutterudites [4], β-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 $CuCu_3V_4O_{12}$ synthesized under a high-pressure [13]. In quadruple perovskites $AA'_3B_4O_{12}$ the A site ions are icosahedrally (twelve neighbors) coordinated by oxygen atoms. The thermal displacement parameter of Cu ions at A site in $CuCu_3V_4O_{12}$ was found to be quite large, $U_{\rm iso} \approx 0.045\,\text{Å}^2$ at 300 K. Together with unusual behavior of specific heat $C_p(T)$ this led to suggestion of possible rattling in $CuCu_3V_4O_{12}$ [13].

In the present paper we report direct evidence of a rattling mode in $CuCu_3V_4O_{12}$ and another recently synthesized quadruple perovskite $CuCu_3Fe_2Re_2O_{12}$. 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 $CuCu_3V_4O_{12}$ and $CuCu_3Fe_2Re_2O_{12}$, respectively, were used.

The crystal structure of quadruple perovskites $AA'_3B_4O_{12}$ on example of $CuCu_3Fe_2Re_2O_{12}$ is shown in Fig. 1a. $CuCu_3V_4O_{12}$ 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 Cu^{1+} ions. Cu ions at A' site have local magnetic moment and these are Jahn–Teller active Cu^{2+} ions.

In $CuCu_3V_4O_{12}$ distance between 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 O_{12} cage, a rattling mode. The dependence of DFT + U total energy on Cu^{1+} displacement has a minimum at ∼0.35 Å distortion. Thus our calculations directly demonstrate presence of the rattling mode in $CuCu_3V_4O_{12}$. 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 $CuCu_3Fe_2Re_2O_{12}$ [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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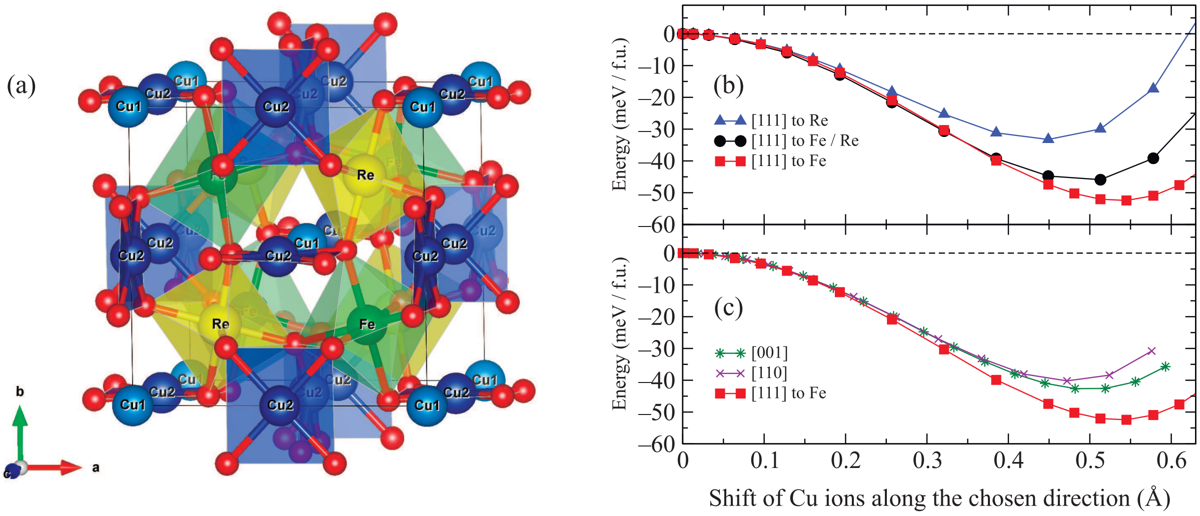

Fig. 1. (Color online) (a) – Crystal structure of quadruple perovskites AA'$_3$B$_4$O$_{12}$ on example of CuCu$_3$Fe$_2$Re$_2$O$_{12}$. There are two types of Cu ions: Cu1 (light blue) is in a large cage, *A* site, and can rattle, while Cu2 (dark blue) is in square-planer coordinated A' site. FeO$_6$ and ReO$_6$ octahedra are shown by yellow and green, respectively. In CuCu$_3$V$_4$O$_{12}$, 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$_3$Fe$_2$Re$_2$O$_{12}$

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$_3$V$_4$O$_{12}$. We predict the same phenomenon in the recently synthesized CuCu$_3$Fe$_2$Re$_2$O$_{12}$. The [111] direction of Cu1 rattling turns out to be the most energetically favourable.

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