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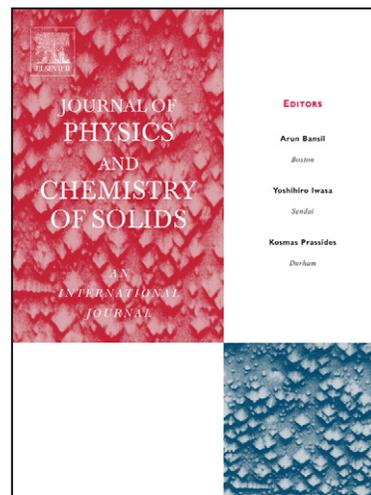
## Author's Accepted Manuscript

*Ab initio* study of the pressure effects on  $R_2Mo_2O_7$

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## Abstract

Structural parameters and Mo 4d bands in geometrically frustrated pyrochlore  $R_2\text{Mo}_2\text{O}_7$  ( $R$ : Nd, Sm, Gd, Tb, Dy) have been studied using *ab initio* methods. Both of chemical pressure and external pressure give linear behaviors of structural parameters. The chemical pressure affects more strongly on Mo–O–Mo bond angle, oxygen coordinate, and lattice constant, whereas one electron band width varies more rapidly with external pressure in good agreement with experimental results.

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Geometrically frustrated pyrochlore materials  $R_2\text{Mo}_2\text{O}_7$  ( $R$ : a rare earth ion,  $Fm\bar{3}m$ ;  $Z = 8$ )<sup>1</sup> have attracted a great attention because of their unusual magnetism behaviors. Experiments evidently show ferromagnetic metallic states (FMM) for  $R = \text{Nd}, \text{Sm}, \text{Gd}$  and spin glass insulating states (SGI) for  $R = \text{Tb}, \text{Dy}, \text{Y}^{2-5}$ . In addition,  $\text{Gd}_{(1-x)}\text{Dy}_x\text{Mo}_2\text{O}_7$  system is demonstrated to be on the boundary of FMM-SGI transition<sup>2</sup>. From the magnetic phase diagram, FMM-SGI transition is thought to be related to the rare earth ionic radius and consequently, structural parameters.

The pyrochlore is composed of two parallel and half of lattice constant displaced sublattices of corner sharing chains of  $R$  and Mo. Mo is surrounded by 6 neighboring O forming a distorted octahedron that changes its shape accompanied by oxygen coordinate  $u$  and Mo-O-Mo bond angle  $\theta$ . There have been several attempts to understand the mechanism of magnetic phase transition in  $R_2\text{Mo}_2\text{O}_7$ . For example, it has been suggested that superexchange interaction should be controlled by the ratio of on-site Coulomb energy  $U_{eff}$  and Hund exchange coupling  $J_H$  in molybdates<sup>6</sup>. In addition, Taguchi et al.<sup>7</sup> observed ferromagnetic characteristics due to the spin chirality and the associated Berry phase of Mo  $4d$  spin.

It is, thus, particularly interesting to understand the mechanism of magnetic phase transition arising from Mo  $4d$  spin. From the synchrotron radiation x-ray powder experiments, it is found that Mo-O-Mo bond angle  $\theta$  is wider for FMM state than SGI state<sup>8</sup>. The bond angle increases with ionic radius  $r_R$  from  $\theta = 129.7^\circ$  for  $\text{Dy}_2\text{Mo}_2\text{O}_7$ (SGI,  $r_R = 1.027 \text{ \AA}$ ) to  $\theta = 131.5^\circ$  for  $\text{Nd}_2\text{Mo}_2\text{O}_7$  (FMM,  $r_R = 1.109 \text{ \AA}$ ). It is important to see that this is opposite to Kanamori-Goodenough rule<sup>9</sup> for antiferromagnetism.

The change of one electron band width  $W$  follows double exchange interaction, negative pressure dependency behavior of the transition temperature,  $dT_c/dP$ , can not be explained by double exchange<sup>10</sup>. Therefore, to understand the magnetic interactions, it is essential to investigate the structural parameter's behaviors against pressures. Recently, it suggested that chemical pressure effect with external pressure gives equivalent effects on structural parameters and magnetic properties<sup>10</sup>. However, it is questionable that chemical pressure gives the same size of effects on the structure as external pressure does.

In this paper, we have performed the total energy calculations. We have used a plane wave basis set with the projector augmented wave (PAW) method<sup>11</sup> as implemented in VASP<sup>12</sup> package. The calculations were based on the generalized gradient approximation given by

Perdew and Wang (PW91)<sup>13</sup> with exchange and correlation potential. We used  $5 \times 5 \times 5$  kpoints mesh in the Brillouin zone with Gamma point centered. The pyrochlore structure is characterized by the cubic space group  $Fm\bar{3}m$ . The unit cell contains 2  $R_2\text{Mo}_2\text{O}_7$  units with R ions at  $16d$ , Mo at  $16c$ , O1 at  $48f$  and O2 at  $8b$ . For chemical pressure, we replaced a lanthanide and made the system relaxed fully. Also, we made each system be relaxed with constant volume for external pressure effect.

Figure 1 shows the relations between  $48f$  oxygen coordinate  $u$  and lattice constant  $a$ . Ishikawa et al.<sup>10</sup> suggested that chemical pressure and external pressure give same lattice constant  $a$  versus oxygen coordinate  $u$  linear relation. Meanwhile, Fig. 1 shows that the linear dependences are different in both cases. In Fig. 1, oxygen coordinate  $u$  linearly decreased with the sharp slope  $-0.027 \text{ \AA}^{-1}$  for chemical pressure compared with other external pressures which have the slope around  $-0.01 \text{ \AA}^{-1}$  on average. We can see that the chemical pressure effects on the relations between  $u$  and  $a$  are much more than external pressures' by 2.7 times. Moreover, concerning the external pressure, the slopes are slightly reduced with increasing ionic radius. For example,  $\text{Nd}_2\text{Mo}_2\text{O}_7$  has the slope of  $-0.010(3) \text{ \AA}^{-1}$  and  $\text{Dy}_2\text{Mo}_2\text{O}_7$  does  $-0.011(2) \text{ \AA}^{-1}$ , which means that  $du/da$  shows not only almost same behaviors on external pressure but also slight differences with respect to the change of ionic radius.

Figure 2 shows  $\theta$  dependence on lattice constant  $a$ , in which chemical pressure takes more

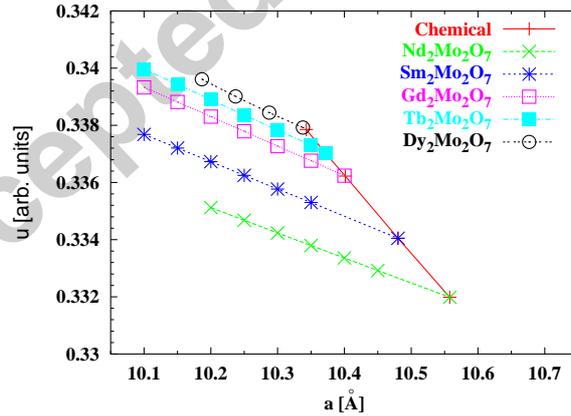


FIG. 1: Oxygen coordinate  $u$  versus lattice constant  $a$  for chemical pressure (red crosses and line) and external pressure on each pyrochlore. From the left upper side of red line each point corresponds to the  $R = \text{Nd}, \text{Sm}, \text{Gd}, \text{Tb}, \text{Dy}$ , respectively.

effects than external pressure on  $\theta$ . Also, with respect to crystallography, Mo–O–Mo bond angle  $\theta$  should be decided by only  $u$ . In the inset of Fig. 2, we showed  $\theta$  dependent on only  $u$  so that both lines of chemical and external pressure follow the exact same line  $\theta(u)$  derived from crystallography. This relations means that  $\theta$  is the function of two variables( $a$ , ionic radius) and the positive slope in the Fig. 2 and negative slope in the inset of Fig. 2 are opposite to Kanamori-Goodenough rule in which wider bond angle prefers antiferromagnetism. Thus, we would address that there is no superexchange interactions in Mo–O–Mo bonds.

We show in Fig. 3 pressure dependences of lattice constant  $a$  and oxygen coordinate  $u$ , respectively. Each lanthanide pyrochlore has similar slope but is different in the absolute values. Fig. 3 (a) shows the relations of lattice constant and applied pressure.  $da/dp$  are  $-0.014(2)$  Å/GPa for  $\text{Nd}_2\text{Mo}_2\text{O}_7$ ,  $-0.015(1)$  Å/GPa for  $\text{Gd}_2\text{Mo}_2\text{O}_7$ ,  $-0.015(1)$  Å/GPa for  $\text{Tb}_2\text{Mo}_2\text{O}_7$  and  $-0.016(5)$  Å/GPa for  $\text{Dy}_2\text{Mo}_2\text{O}_7$ , respectively. The slope  $da/dp$  is getting steeper with decreasing ionic radius of lanthanide. Thus, external pressure changes lattice constant more on smaller ionic radius lanthanide.

Fig. 3 (b) shows oxygen coordinates' linear behaviors against applied pressures of different kinds of lanthanide pyrochlores. The lines in the figure are almost parallel each other and have the pressure coefficient ( $= du/dp$ ) are  $1.24 \times 10^{-4}$  GPa $^{-1}$  for  $\text{Nd}_2\text{Mo}_2\text{O}_7$ ,  $1.55 \times$

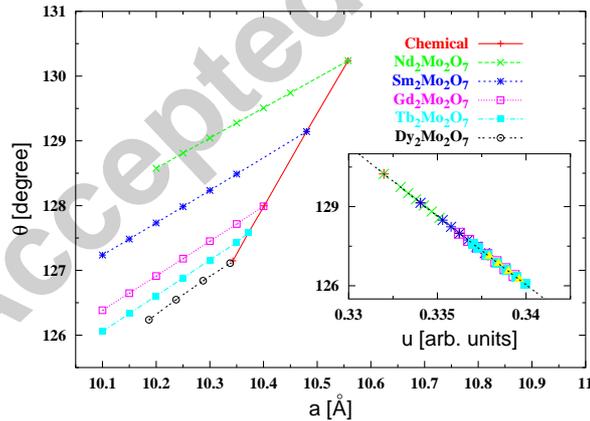


FIG. 2: The relations of Mo–O–Mo bond angle  $\theta$  and lattice constant  $a$  are shown. The highest slope line(red) correspond to the chemical pressure. The inset shows  $u$  dependence of  $\theta$ . The straight dashed line in the inset results from crystallographic data.

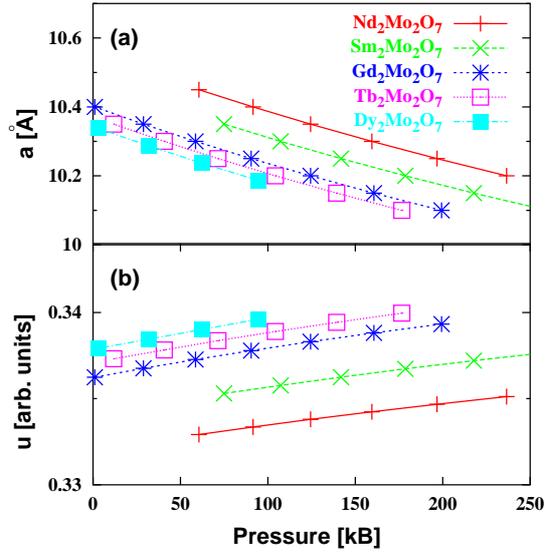


FIG. 3: (a) Lattice constant and (b) oxygen coordinate against external pressure. The straight lines in (a) and (b) are the results of the least-square-fitting.

$10^{-4} \text{ GPa}^{-1}$  for  $\text{Gd}_2\text{Mo}_2\text{O}_7$ ,  $1.61 \times 10^{-4} \text{ GPa}^{-1}$  for  $\text{Tb}_2\text{Mo}_2\text{O}_7$ ,  $1.84 \times 10^{-4} \text{ GPa}^{-1}$  for  $\text{Dy}_2\text{Mo}_2\text{O}_7$ , respectively.

The slopes  $da/dp$  and  $du/dp$  in the Fig. 3 are good agreement with experimental data ( $da/dp = -0.016(3) \text{ \AA GPa}^{-1}$ ,  $du/dp = 1.78 \times 10^{-4} \text{ GPa}^{-1}$ ) but getting steeper with decreasing ionic radius of lanthanide. Thus, external pressure changes lattice constant and nearest Mo–O distance more on smaller ionic radius lanthanide.

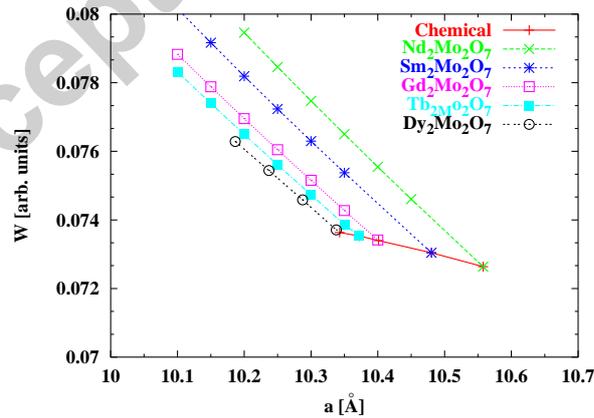


FIG. 4: One electron band width  $W$  versus lattice constant  $a$  are shown. One electron band width  $W$  rely on more external pressure than chemical pressure

In Fig. 4, we plotted one electron band width( $W$ ),  $\cos((\pi - \theta)/2) \cdot d^{-3.5}$ , of Mo–O–Mo bond against lattice constant  $a$ . We can see that the chemical pressures do not give so much contribution to the  $W$  as external pressures do and increasing  $W$  with pressure, which are consistent results of experimental data<sup>10</sup>, implies pressure effects enhance double exchange.

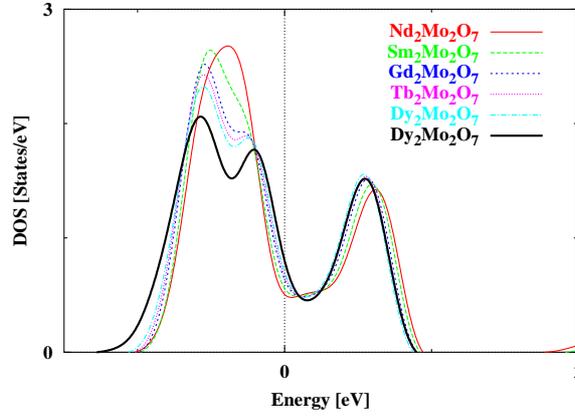


FIG. 5: The spin-up density of states(DOS) of  $4d$  Mo versus energy are shown. the black colored solid line corresponds to  $\text{Dy}_2\text{Mo}_2\text{O}_7$  with external pressure(94.7 kBar). At the Fermi level, We can see DOS become higher with pressure effect. The band width corresponding to lower  $t_{2g}$  bands also become wider. From  $\text{Gd}_2\text{Mo}_2\text{O}_7$ , the lower  $t_{2g}$  gets to split into two peaks

In Fig 5, we draw spin-up  $t_{2g}$  bands of Mo  $4d$  while Fermi level is set to zero energy. All of spin-down  $t_{2g}$  bands are empty and located at higher states than Fermi level. We can see that the DOS at the Fermi level grows gradually as pressure goes up. The width of occupied  $t_{2g}$  bands become wider with pressure. This indicate that conduction of Mo  $4d$  electrons becomes easier when pressure is increased as is understood from usual thought in a metallic system. The increased DOS at the Fermi level explains more electrons can participates in conduction by the double exchange mechanism. Moreover, the variation of DOS shapes shows that weak Jahn–Teller distortion occurs.

Although the double exchange is strengthened by pressures, experiments show that  $\text{Gd}_2\text{Mo}_2\text{O}_7$  undergoes magnetic phase transition from FMM to SGI with chemical/ external pressure. This means that antiferromagnetic ordering by superexchange interaction is dominant even though double exchange is enhanced with increased pressure<sup>14</sup>.

Indeed, Neutron scattering measurements suggest an important role of superexchange interactions between lanthanide  $4f$  electrons and Mo  $4d$  electrons<sup>7</sup>. They explain that

double exchange is governed by itinerant  $4d$  electrons while localized Nd  $4f$  electrons gives superexchange interaction via coupling to Mo  $4d$ . Therefore, we may refer the magnetic ordering of  $R_2\text{Mo}_2\text{O}_7$  is due to the competition between the enhanced ferromagnetic ordering of Mo  $4d$  and antiferromagnetic ordering of lanthanide  $4f$ .

In summary, using *ab initio* methods, we systematically investigated the dependences of Mo–O–Mo bond angle, lattice constants, and oxygen coordinate of different lanthanide pyrochlores  $R_2\text{Mo}_2\text{O}_7$  on both of chemical and external pressure. Our study shows that most relations between structural parameters follow linear lines but different with the ionic radius of lanthanide. One electron band width shows the hopping rate increases with pressure, with which we would address that double exchange is enhanced. The change of  $4d$  Mo bands shapes also indicates the increasing ferromagnetism. Thus, SGI states in lanthanide pyrochlores could be explained in terms of much stronger superexchange than enhanced double exchange.

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