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Lattice Relaxation Effects on the Multiplet Energies of Ruby Under Pressure using One-Electron Calculations

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Abstract. Up to recently, it has been difficult to calculate the multiplet energies of compounds using one-electron approach. Since it only considers one electron and one nuclei, the interaction among the electrons are neglected. Previously we have successfully estimated the $^2E \rightarrow {}^4A_2$ (R-line) levels of ruby at 0 pressure using one-electron approach based on one-electron calculation using the first-principles Discrete Variational-Xα (DV-Xα) method. Here we want to perform similar investigation, not only for 0 pressure but up to 110 GPa. We estimated the lattice relaxation effect due to the Cr^{3+} substitution and due to the applied pressure by using two different methods i.e., Shannon's crystal radii and geometry optimizations. Two different types of model cluster consisting of 7 and 63 atoms will be used. The ^2E level is estimated by the barycenter of t_{2g}^3 configuration which consists of 4 multiplets.

1. Introduction

Up to recently, it has been difficult to calculate the multiplet energies of compounds using one-electron approach. Since it only considers one electron and one nuclei, the interaction among the electrons are neglected. Previously we have successfully carried out a comparative study on the transition energies from ^2E to $^4A_2$ (R-line) and from $^4A_2$ to $^4T_2$ (U-band) of α-Al_2O_3: Cr^{3+}, or the so-called ruby, at zero pressure based on one-electron [1] and many-electron first-principles calculations [2]. The estimations were performed without relating to any observed parameter. In Ref. 1, we introduced the improved formula to calculate the R-line energy. Based on Ohnishi's work [3], the R-line energy was estimated by the barycenter of t_{2g}^3 configuration which consists of 3 multiplets i.e., ^2E, $^2T_1$, and $^2T_2$ states. Whereas the U-band energy were simply estimated to be equal to the crystal field splitting, 10*Dq*. However, according to the ligand filed theory (LFT), the t_{2g}^3 configuration may consist of 4 multiplet states; not only ^2E, $^2T_1$, and $^2T_2$ states but also $^4A_2$ state [4, 5]. On the other hand, in the case of U-band energies and 10*Dq,* they have the distinctly different estimations. In the other papers, we also reported an investigation on the effect of lattice relaxation on the bond length and the molecular orbital energy

[6,7]. The effect of lattice relaxation was estimated by applying pressure for ca. 0-110 GPa. It was performed by the first-principles band-structure calculations using the Cambridge Serial Total Energy Package (CASTEP) code [6]. The results show that when we applied pressure on ruby, the bond length decreased rapidly. On the other hand, the molecular orbital energy was estimated from the one-electron calculation using the first-principles Discrete Variational-Xα (DV-Xα) method [7]. The results show that both t_{2g} and e_g levels of $3d^3$ orbital increased. The crystal field splitting ($10Dq$) especially increased as the pressure increased.

In this paper, we want to perform similar investigation, not only for 0 pressure but up to 110 GPa. This work aims to find out the consistency of our previous results in Ref. 1 for ruby under pressure. Here we also compared the lattice relaxation effect estimated using Shannon's crystal radii and geometry optimizations. Two different types of model cluster consisting of 7 and 63 atoms were used.

2. Computational Method

The model clusters used in this work is similar with those used in Ref. 1. We constructed two sizes of model clusters i.e., 7- and 63-atom. These model clusters were treated without and with considering lattice relaxation effect. The model clusters including lattice relaxation effect were estimated based on Shannon's crystal radii method [8, 9] and geometry optimization method using the Cambridge Serial Total Energy Package (CASTEP) code in the Material Studio 6.0 [10-12]. Those model clusters were pressed from 0 to 110 GPa. The procedure of these steps were explained in Ref. 6. In order to estimate the multiplet energy levels such as R-line and U-band energies of ruby using the one-electron method, here we used DV-Xα method similar with those used in Ref. 1. Figure 1 illustrates the estimation of the energy levels of ruby. In the $3d^3$ configuration, there are several multiplets such as $^4A_2$, ^2E, $^2T_1$, $^2T_2$, and $^4T_2$ states. In the term of Racah parameter, the energies of $^4A_2$, ^2E, and $^4T_2$ can be described as -15B, -6B+3C, and -15B+10Dq, respectively [13]. The R-line energy was estimated by $\varepsilon(2E) = 0.9 \times \Delta E_R$, where $\Delta E_R = \frac{10}{3}(3B + C)$. On the other hand, the U-band energy ($\varepsilon(4T2)$) was simply calculated as $\Delta E_U = 10Dq$.

3. Results and discussion

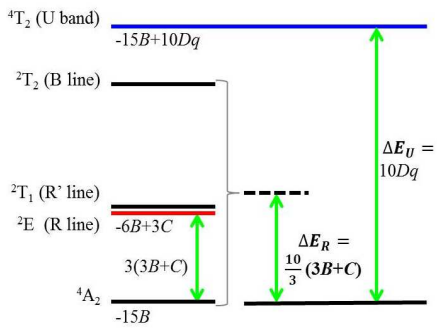

Figure 1. Schematic illustration on the estimation of R-line and U-band energy of ruby based on one-electron calculations.

Figure 1 shows the estimated R-line and U-band energies of ruby under pressure. Figure 1(a), 1(b) and 1(c) are obtained from the 7-atom model clusters. On the other hand, Figure 1(d), 1(e) and 1(f) are obtained from the 63-atom model clusters. The top panel of Figure 1 (a and d) shows the estimated multiplet energies of ruby under pressure without considering any lattice relaxation effect. The middle panel of Figure 1 (b and e) shows the estimated multiplet energies of ruby under pressure with considering lattice relaxation effect based on Shannon's crystal radii. Whereas the lowest panel of Figure 1 (c and f) shows the estimated multiplet energies of ruby under pressure with considering lattice relaxation effect based on geometry optimization using CASTEP code. The R-line and U-band

energies are shown by circle (●) and square (■) symbols. The theoretical results are shown by coloured symbols connected with solid line, while the experimental data obtained from Ref. 14-17 are shown by black symbols without any line.

The estimated R-line energies obtained from all model clusters decreased as the pressure increased. It is also shown that by calculations using 7-atom model clusters, the R-line energies were overestimated. However, the agreement has been improved excellently by using larger clusters, 63-atom model clusters. Unlike the R-line energies which were found to slightly decrease along with the increasing pressure, the U-band energies were increased. The estimated U-band energies agree with the experimental data only by the model cluster without considering the lattice relaxation effect, both 7- an d63-atom model clusters. When the lattice relaxation effect was considered, the U-band energies seem to be underestimated. Compared to the results obtained from the model clusters with considering lattice relaxation based on Shannon's crystal radii, the results obtained from the model clusters with considering lattice relaxation based on geometry optimization using CASTEP code give better agreement. The increasing of U-band energy, which is actually 10*Dq* in this work, is due to the decreasing of Cr-O bond length as the result of applying pressure.

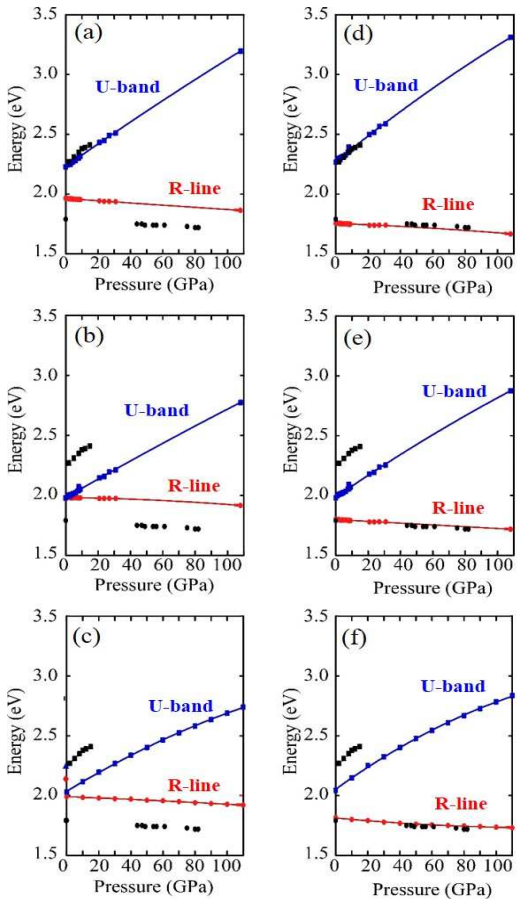

Figure 2. The estimated R-line and U-band energies based on (a) 7-atom model clusters without considering lattice relaxation effect (b) 7-atom model clusters with considering lattice relaxation effect based on Shannon's crystal radii (c) 7-atom model clusters without considering lattice relaxation effect based on geometry optimization using CASTEP code (d) 63-atom model clusters without considering lattice relaxation effect (e) 63-atom model clusters with considering lattice relaxation effect based on Shannon's crystal radii and (d) 63-atom model clusters without considering lattice relaxation effect based on geometry optimization using CASTEP code. The black symbols are the experimental data obtained from Ref. 14-17.

4. Conclusion

We have successfully calculated the multiplet energy levels of ruby bond length under pressure without referring to any experimental parameter using the one-electron first-principles calculations, DV-Xα method. The lattice relaxation effects were calculated by two different methods *i.e.*, the first-principles band-structure calculations using Shannon's crystal radii method and CASTEP method. The results show that the R-line energies decrease as the pressure increase. On the other hand, the U-band energies increase as the pressure increase. The investigation on the cluster size dependence shows that the larger size of cluster improves the accuracy of R-line energies. On the other hand, the increasing of U-band energy, which is actually 10*Dq* in this work, is due to the decreasing of Cr-O bond length as the result of applying pressure. Although the calculation based on 7-atom model clusters gives better agreement with experiment, the underestimation on the barycenter of t_{2g}^3 configuration cannot be neglected. This result also implies that the size of model cluster is crucial.

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