Prediction of Pressure Dependence of R-line Emission for d^3 Ions in α-Al_2O_3 Based on First-Principles Calculations

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1. Introduction

First-principles calculation of the pressure dependence of the optical transitions of Cr^{3+} in α-Al_2O_3 was performed by Duan *et al.* in 1998 [1]. They successfully reproduced the redshifts of the $^4A_2 \rightarrow {}^2E$ (R-line) transition energy and the blueshifts of both $^4A_2 \rightarrow {}^4T_2$ (U-band) and $^4A_2 \rightarrow {}^4T_1$ (Y-band) transition energies induced by pressure [1]. However, the investigation of pressure dependence on other d^3 ions such as Mn^{4+}, which is drawing much attention as the activator ion in red phosphors for white LED devices, has not been reported. In order to establish a guideline to design a novel Mn-doped red phosphor, it is important to clarify the relationship between the local structure around the activator ion and the optical spectra. In order to clarify the relationships between the local structure and the R-line energy, we performed first-principles calculations of the pressure dependence of d^3 ions in α-Al_2O_3 crystals using the discrete variational multielectron (DVME) method [2] and investigated the factors to determine the R-line energy in detail.

2. Computational method

Molecular orbital calculations were performed based on the discrete variational-Xα (DV-Xα) method, while the multiplet energy calculations were performed based on the DVME method developed by Ogasawara *et al.* [2]. As corrections, we used configuration dependent correction (CDC) and correlation correction (CC), which represent the effect of electron correlations on the crystal-field splitting and on the spin-flip transition energy, respectively. In this approach the diagonal matrix elements of the Hamiltonian for the *p*th state are expressed as

$$H_{pp}{}^{CDC} = H_{pp} + D^{CDC}(m,n), \qquad (1)$$

where $D^{CDC}(m,n)$ is the correction term depending on the configuration $(t_{2g})^m$ $(e_g)^n$ of the *p*th state. On the other hand, the consideration of CC is equivalent to an approximation to use the following effective Hamiltonian.

$$H = \sum_{i=1}^{n} h(\mathbf{r}_i) + \sum_{i=1}^{n}\sum_{j>i}^{n} \frac{c}{r_{ij}}. \qquad (2)$$

where *c* is the CC factor. We constructed model clusters consisting of 63 atoms with C_3 symmetry based on the crystal structure of α-Al_2O_3 which has a hexagonal A_2X_3 structure (space group $R\bar{3}c$). For the crystal structures under pressure, the experimental data reported by Finger [3] were used.

3. Results and discussion

Figure 1 shows the relation between pressure (MPa) and the calculated R-line energy (eV) with and without corrections (CDC and CC). The results show that when the CDC and CC are not considered, the R-line energy increases rapidly as pressure increases, which is the opposite to the observed tendency. On the other hand, it is clearly shown that the tendency is reversed when CDC and CC are considered. As a result, the experimental tendency was reproduced well from first-principles calculations. Similarly, the pressure dependence of R-line energy for Mn^{4+} in α-Al_2O_3 was also predicted from first principles.

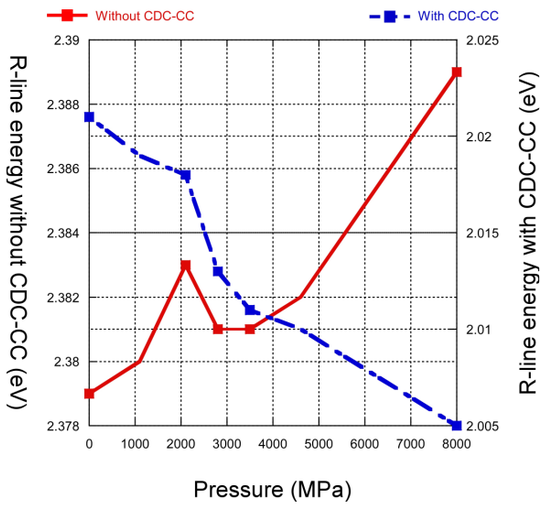

Fig. 1. Pressure dependence of the calculated R-line emission energy with and without CDC and CC (CDC-CC), represented by solid and dashed line respectively.

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