Improved Multiplet Energy Diagrams for d^3 ions in Oxides Based on Correlation Corrections

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1. Introduction

The transition metal (TM) d^3 ions have been widely studied as activator ions for luminescent materials such as phosphors and solid-state lasers. The so called Tanabe-Sugano diagrams are quite useful for the analysis of the multiplet energy levels of TM ions in crystals. However, they cannot be used for the quantitative prediction of the multiplet energy levels since these diagrams include empirical parameters to be determined by the experimental spectra. A more practical energy diagram without any empirical parameters is desired for the theoretical search of novel luminescent materials. In order to develop a practical energy level diagram which can be used for theoretical material design, we have recently created diagrams based on the bond length [1]. However, in the diagram for Cr^{3+} in oxides, the R-line energy increases as the bond length decreases, which is opposite to the observed tendency. In this work, in order to improve these diagrams, we introduced some corrections such as the configuration-dependent correction (CDC) and the correlation correction (CC). The effects of these corrections on the multiplet energy levels were investigated in detail.

2. Computational method

We constructed model clusters TMO_6 (TM=Cr, Mn) consisting of 7 atoms with O_h symmetry, where the TM-O bond length was gradually changed. The multiplet energy calculations were performed based on the discrete variational multielectron (DVME) method [2]. In order to improve the results, we also considered 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 pth 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 pth 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.

3. Results and discussion

The multiplet energy diagram for CrO_6 clusters obtained by the first-principles calculations with CDC and CC is shown in Fig. 1. Compared to the diagram calculated without CDC and CC, the tendency of the ^2E_g and $^2T_{1g}$ is reversed and they clearly decrease as the bond length decreases. Since this tendency is consistent with the experimentally observed pressure dependence of the R-line emission energy for ruby, the results indicated that the consideration of the corrections such as CDC and CC is critical for the prediction of the R-line emission energy based on first-principles calculations.
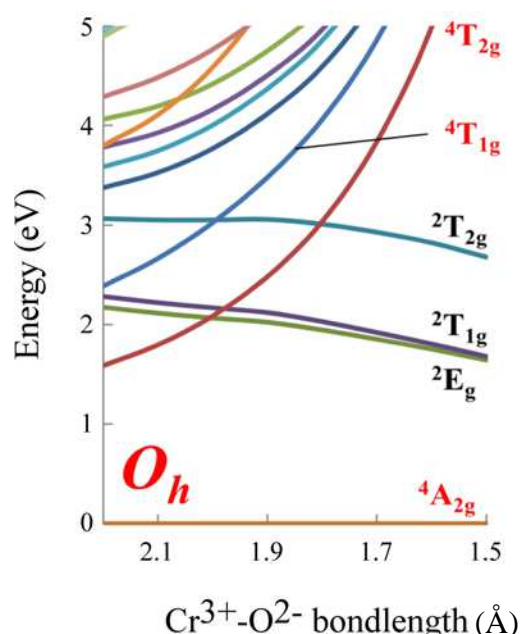

Fig. 1. Improved multiplet energy diagram for Cr^{3+} in oxides with O_h symmetry with consideration of CDC and CC.

REFERENCES

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