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Kyoto University
Multiplet structures of tetrahedrally coordinated Cr\textsuperscript{4+} and Cr\textsuperscript{5+} in Y\textsubscript{3}Al\textsubscript{5}O\textsubscript{12}

Takugo Ishii, a) Kazuyoshi Ogasawara, and Hirohiko Adachi
Department of Materials Science and Engineering, Kyoto University, Sakyo, Kyoto 606-8501, Japan
Isao Tanaka
Department of Energy Science and Technology, Kyoto University, Sakyo, Kyoto 606-8501, Japan

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Multiplet structures of tetrahedrally coordinated Cr\textsuperscript{4+} and Cr\textsuperscript{5+} in Y\textsubscript{3}Al\textsubscript{5}O\textsubscript{12} (yttrium aluminum garnet) were calculated with use of the ab initio electronic-structure calculation method. The calculated absorption spectrum of Cr\textsuperscript{4+} showed that two bands at the near-infrared and visible spectral regions originated from the same \(3T\textsubscript{1}\) parent multiplet term. The calculated levels originating from Cr\textsuperscript{5+} in the near-infrared region overlapped with the levels originating from Cr\textsuperscript{4+}. Both the lowest-spin-allowed transitions of Cr\textsuperscript{4+} and Cr\textsuperscript{5+} were revealed to have the same polarization dependence. The result indicated that confusion on the assignment of the peaks could be ignored if the Cr\textsuperscript{5+} state really exists. © 2001 American Institute of Physics. [DOI: 10.1063/1.1364655]

We report the results obtained from the ab initio calculation of multiplet structures of tetrahedrally coordinated Cr\textsuperscript{4+} and Cr\textsuperscript{5+} in Y\textsubscript{3}Al\textsubscript{5}O\textsubscript{12} [yttrium aluminum garnet (YAG)] crystal. First, we show that the revised assignment of the absorption spectrum proposed by Eilers et al.\textsuperscript{1} was valid as regards the conclusion that both dominant bands located at the near-infrared (NIR) and visible regions originated from the transitions to the states which belong to the same \(3T\textsubscript{1}\) parent multiplet term of tetrahedrally coordinated Cr\textsuperscript{4+}. Second, we predict the absorption peak energies of tetrahedrally coordinated Cr\textsuperscript{4+} and Cr\textsuperscript{5+}. We propose a possibility that the lowest-spin-allowed transition of Cr\textsuperscript{5+} could be confused with that of Cr\textsuperscript{4+} in the NIR region.

Cr\textsuperscript{4+}-doped crystals have been studied in the research field of solid-state lasers with NIR emission. One well-investigated Cr\textsuperscript{4+} laser crystal is Cr-doped YAG. However, the assignment of the ground-state absorption spectrum of Cr\textsuperscript{4+}:YAG has been controversial. In early years, the two broad bands at the NIR and visible spectral regions had been assigned to the transitions in different \(3T\textsubscript{2}\) and \(3T\textsubscript{1}\) parent multiplet terms, respectively.\textsuperscript{2} But, another assignment was proposed by Eilers et al., who pointed out that both bands should originate from the transitions to the states in the same \(3T\textsubscript{1}\) parent multiplet term with large energy splitting.\textsuperscript{1} Why did such ambiguity exist in understanding the absorption spectra? Classical semiempirical analysis methods, which were often based on ligand field theory,\textsuperscript{3} required us to stand on our assumption to determine the adjustable parameters. To avoid ambiguity in determining the parameters, we have to depend on ab initio methods. In Cr\textsuperscript{4+}:YAG, only a few studies have been done based on ab initio electronic-structure calculation methods. Sobolev et al.\textsuperscript{4} gave a simple discussion concerning the valence state of chromium by a cluster method.\textsuperscript{5} Ching, Xu, and Brideken conducted the band calculations, and proposed a model associated with excited-state absorption.\textsuperscript{6} Those methods, however, lied under the framework of a one-electron approximation, and we could not directly obtain the multiplet structures which require us to perform a many-electron calculation.

We have been developing a general ab initio method, the discrete variational multielectron (DVME) method for direct calculation of electronic structures that involve multiplet structures produced by impurity metals.\textsuperscript{6} As for the Cr\textsuperscript{4+} system, we had already confirmed that the method reproduced the large energy splittings within the \(3T\textsubscript{1}\) parent multiplet term (\(>3000 \text{ cm}^{-1}\)) and the polarization dependence of the intensity derived from the low \(C\textsubscript{s}\) symmetry at the Cr\textsuperscript{4+} site in the absorption spectrum of Cr\textsuperscript{4+}:Ca\textsubscript{3}GeO\textsubscript{4}.\textsuperscript{7} The characteristic feature of the DVME method compared to the traditional methods based on ligand field theory is that we can obtain such large energy splittings under low symmetry, which has been a question regarding the Cr\textsuperscript{4+}-doped system, without introducing any adjustable parameters. Since the details of the DVME method had been already written in Ref. 6, only the essence is explained below.

First, in the computational procedure one-electron molecular orbital calculation based on density functional theory, on which many contemporary one-electron ab initio methods are dependent, is conducted with the SCAT code.\textsuperscript{8} Next, the impurity-level molecular orbitals, which are mainly composed of the Cr 3d orbital, are taken out to construct the wave functions of the many-electron system in expression of the linear combination of Slater determinants. One difference of the DVME method from traditional semiempirical methods based on ligand field theory is that two-electron integrals are numerically calculated, not analytically. This numerical approach enables us to universally apply the method to the system with any symmetry and with any electron configuration. The present study was performed by a nonrelativistic version for simplification. The spin-orbit coupling parameter, which describes the primary relativistic effect, is small.
The calculated energies of some excited states were compared with the theoretically obtained absorption spectrum in the NIR–visible bands. Riley et al. pointed out from their semiempirical analysis that the energy splitting within the \( \text{S}_1 \) multiplet term should be large enough to produce both the apparent NIR and visible bands. Riley et al. also concluded that the NIR absorption band was produced by the \( 3B(3A_2) \rightarrow 3A'(T_{1}) \) transition of the tetrahedrally coordinated \( \text{Cr}^{4+} \). Thus, we agree with Eilers’ conclusion that the energy splitting within the \( 3T_{1} \) multiplet term is large enough to produce both the apparent NIR and visible bands. Riley et al. pointed out from their semiempirical analysis that the energy splitting within the \( 1E \) multiplet term should be large, at more than 1000 cm\(^{-1}\), and the assignment concerning the \( 1E \) multiplet term proposed by Eilers et al. with only a 28 cm\(^{-1}\) splitting was invalid.  

The calculated energies of the states located at the NIR region obtained from \( \text{Cr}^{4+} \) and \( \text{Cr}^{5+} \) cluster models are shown in Figs. 3(a) and 3(b), respectively. Comparing the results in Figs. 3(a) and 3(b), we see that the excited states well overlap each other. There have been several studies that indicated the existence of \( \text{Cr}^{5+} \) in the \( \text{Cr}^{4+} \)-doped system. Reinen et al. studied diffuse reflectance spectra of Cr-doped \( \text{Ca}_3\text{PO}_4\text{Cl} \) and \( \text{Ca}_5(\text{PO}_4)_3\text{Cl} \), which had tetrahedrally coordinated sites. They revealed that the \( \text{Cr}^{5+} \)-like spectrum had specific bands in the 10 000–13 000 cm\(^{-1}\) region, which overlapped with the bands in the \( \text{Cr}^{4+} \)-like spectrum. Reinen et al. studied diffuse reflectance spectra of Cr-doped \( \text{Li}_2\text{MgSiO}_4 \), and attributed the band to the \( 2E \rightarrow 2T_{1g} \) transition of \( \text{Cr}^{5+} \). Our calculated energy of the \( 3B(3A_2) \rightarrow 3A'(T_{1}) \) transition of the tetrahedrally coordinated \( \text{Cr}^{4+} \) is in good agreement with the experimentally deduced one. Although the symmetry was low, transitions to the states in \( 3T_{2} \) multiplet term, in which the transition was originally electric-dipole forbidden in the parent \( T_{d} \) symmetry, had no significant transition probability to produce the NIR band in our calculated result. By these facts, we confirmed from the \( ab initio \) calculation that the dominant NIR absorption band was produced by the \( 3B(3A_2) \rightarrow 3A'(T_{1}) \) transition of the tetrahedrally coordinated \( \text{Cr}^{4+} \). Thus, we agree with Eilers’ conclusion that the energy splitting within the \( 3T_{1} \) multiplet term is large enough to produce both the apparent NIR and visible bands. Riley et al. pointed out from their semiempirical analysis that the energy splitting within the \( 1E \) multiplet term should be large, at more than 1000 cm\(^{-1}\), and the assignment concerning the \( 1E \) multiplet term proposed by Eilers et al. with only a 28 cm\(^{-1}\) splitting was invalid. 

We obtained energy splitting at 1290 cm\(^{-1}\). We agree with Riley’s conclusion as far as the magnitude of the energy splitting within \( 1E \) multiplet term is concerned. We consider that the doublet structure with energy splitting of 28 cm\(^{-1}\) in Eilers’ result originated from spin-orbit coupling.

The calculated energies of the states located at the NIR region obtained from \( \text{Cr}^{4+} \) and \( \text{Cr}^{5+} \) cluster models are shown in Figs. 3(a) and 3(b), respectively. Comparing the results in Figs. 3(a) and 3(b), we see that the excited states well overlap each other. There have been several studies that indicated the existence of \( \text{Cr}^{5+} \) in the \( \text{Cr}^{4+} \)-doped system. Reinen et al. studied diffuse reflectance spectra of Cr-doped \( \text{Ca}_3\text{PO}_4\text{Cl} \) and \( \text{Ca}_5(\text{PO}_4)_3\text{Cl} \), which had tetrahedrally coordinated sites. They revealed that the \( \text{Cr}^{5+} \)-like spectrum had specific bands in the 10 000–13 000 cm\(^{-1}\) region, which overlapped with the bands in the \( \text{Cr}^{4+} \)-like spectrum. Reinen et al. studied diffuse reflectance spectra of Cr-doped \( \text{Ca}_3\text{PO}_4\text{Cl} \) and \( \text{Ca}_5(\text{PO}_4)_3\text{Cl} \), which had tetrahedrally coordinated sites. They revealed that the \( \text{Cr}^{5+} \)-like spectrum had specific bands in the 10 000–13 000 cm\(^{-1}\) region, which overlapped with the bands in the \( \text{Cr}^{4+} \)-like spectrum.
$2E(2T_2)$ state at 11330 cm$^{-1}$ in Fig. 3(b) agreed well with those descriptions based on the experimentally obtained results. We propose the possibility that the tail of the NIR absorption band of the so-called Cr$^{4+}$:YAG is composed of at least two absorptions attributed to the $3B(3A_2)\rightarrow3P(3T_1)$ transition of tetrahedrally coordinated Cr$^{4+}$ and to the $2B(2E)\rightarrow2E(2T_2)$ transition of tetrahedrally coordinated Cr$^{5+}$, if the Cr$^{5+}$ state really exists.

Confusing states in the NIR region are the $3B(3T_2)$ state of Cr$^{4+}$ and the $2B(2T_2)$ state of Cr$^{4+}$. Both states should be located below 10000 cm$^{-1}$ in the same energy region. Both the $3B(3A_2)\rightarrow3P(3T_1)$ and $2B(2E)\rightarrow2P(2T_2)$ transitions are spin allowed and electric-dipole forbidden, and have the same polarization dependence under the $S_4$ symmetry. The $3B(3T_2)$ and $2B(2T_2)$ states could be situated at even closer energy than indicated in Figs. 3(a) and 3(b), since we neglected the static lattice relaxation due to substitution of chromium ions for aluminum ions with a different ionic radius. We estimated the average effect of the lattice relaxation on the calculated multiplet energies by the simplest (CrO$_4$) cluster models with different Cr–O bond lengths. The magnitude of the relaxation of the Cr–O bond length estimated by ionic radii were +1.1% for Cr$^{4+}$ and -2.5% for Cr$^{5+}$ based on the original Al–O bond length. The corresponding energy shifts were -240 cm$^{-1}$ for the $3B(3T_2)$ state of Cr$^{4+}$ and +730 cm$^{-1}$ for the $2B(2T_2)$ state of Cr$^{5+}$. This means that the peaks in the absorption spectrum originating from the two transitions should be difficult to distinguish from each other by some experimental methods whose analyses are based on the polarization dependence of the transitions. Eilers et al. had well investigated especially the weak zero-phonon lines at 1280 nm (7814 cm$^{-1}$) by polarization-dependent emission spectroscopy.$^1$ They attributed the zero-phonon lines to the $3B(3A_2)\rightarrow3B(3T_2)$ transition of Cr$^{4+}$. Most studies until now seem to have followed the Eilers’ assignment. We still propose, however, another possibility that the weak zero-phonon lines at 1280 nm (or other satellite lines around them) should be attributed to the $2B(2E)\rightarrow2B(2T_2)$ transition of Cr$^{4+}$. There has been no study that discussed the existence of Cr$^{5+}$ in Cr$^{4+}$:YAG, although the existence had been already observed in garnet, Cr$_3$Ga$_5$Ga$_5$Ge$_5$O$_{12}$.$^1$ We hope further experimental investigations will follow to reconfirm the assignment of the peaks in the absorption spectra of the Cr$^{4+}$-doped system.

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