Multiplet structures of tetrahedrally coordinated Cr\(^{4+}\) and Cr\(^{5+}\) in Y\(_3\)Al\(_5\)O\(_{12}\)

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\(^{4+}\) and Cr\(^{5+}\) in Y\(_3\)Al\(_5\)O\(_{12}\) (yttrium aluminum garnet) were calculated with use of the \textit{ab initio} electronic-structure calculation method. The calculated absorption spectrum of Cr\(^{4+}\) showed that two bands at the near-infrared and visible spectral regions originated from the same \(3T\_1\) parent multiplet term. The calculated levels originating from Cr\(^{5+}\) in the near-infrared region overlapped with the levels originating from Cr\(^{4+}\). Both the lowest-spin-allowed transitions of Cr\(^{4+}\) and Cr\(^{5+}\) 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\(^{5+}\) state really exists. © 2001 American Institute of Physics.

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We report the results obtained from the \textit{ab initio} calculation of multiplet structures of tetrahedrally coordinated Cr\(^{4+}\) and Cr\(^{5+}\) in Y\(_3\)Al\(_5\)O\(_{12}\) [yttrium aluminum garnet (YAG)] crystal. First, we show that the revised assignment of the absorption spectrum proposed by Eilers \textit{et al.}\(^1\) 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 \(3T\_1\) parent multiplet term of tetrahedrally coordinated Cr\(^{4+}\). Second, we predict the absorption peak energies of tetrahedrally coordinated Cr\(^{4+}\) and Cr\(^{5+}\). We propose a possibility that the lowest-spin-allowed transition of Cr\(^{5+}\) could be confused with that of Cr\(^{4+}\) in the NIR region.

Cr\(^{4+}\)-doped crystals have been studied in the research field of solid-state lasers with NIR emission. One well-investigated Cr\(^{4+}\) laser crystal is Cr-doped YAG. However, the assignment of the ground-state absorption spectrum of Cr\(^{4+}\):YAG has been controversial. In early years, the two broad bands at the NIR and visible spectral regions had been assigned to the transitions to the states in different \(3T\_2\) and \(3T\_1\) parent multiplet terms, respectively.\(^2\) But, another assignment was proposed by Eilers \textit{et al.}, who pointed out that both bands should originate from the transitions to the states in the same \(3T\_1\) parent multiplet term with large energy splitting.\(^1\) Why did such ambiguity exist in understanding the absorption spectra? Classical semiempirical analysis methods, which were often based on ligand field theory,\(^3\) required us to stand on our assumption to determine the adjustable parameters. To avoid ambiguity in determining the parameters, we have to depend on \textit{ab initio} methods. In Cr\(^{4+}\):YAG, only a few studies have been done based on \textit{ab initio} electronic-structure calculation methods. Sobolev \textit{et al.} gave a simple discussion concerning the valence state of chromium by a cluster method.\(^4\) Ching, Xu, and Briceken conducted the band calculations, and proposed a model associated with excited-state absorption.\(^5\) Those methods, however, lay 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 \textit{ab initio} method, the discrete variational multielectron (DVME) method for direct calculation of electronic structures that involve multiplet structures produced by impurity metals.\(^6\) As for the Cr\(^{4+}\) system, we had already confirmed that the method reproduced the large energy splittings within the \(3T\_1\) parent multiplet term (>3000 cm\(^{-1}\)) and the polarization dependence of the intensity derived from the low \(C\_s\) symmetry at the Cr\(^{4+}\) site in the absorption spectrum of Cr\(^{4+}\):Ca\(_3\)GeO\(_4\).\(^7\) 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\(^{4+}\)-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 \textit{ab initio} methods are dependent, is conducted with the SCAT code.\(^8\) 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.

\footnote{Electronic mail: tack@cms.mtl.kyoto-u.ac.jp}
enough (<500 cm\(^{-1}\)) for a Cr ion, compared to the magnitude of energy splitting within the parent \(3T_1\) multiplet term on which we focus in this study.

The YAG crystal belongs to the garnet-type structure in the cubic system. It has been commonly said that the dominant bands in the absorption spectrum in the NIR-visible region, up to about 18 000 cm\(^{-1}\), are produced mainly by tetrahedrally coordinated Cr\(^{4+}\). In this study, we used \((\text{CrY}_6\text{Al}_4\text{O}_{44})^{54}\) and \((\text{CrY}_6\text{Al}_4\text{O}_{44})^{53}\) cluster models for calculation of the multiplet structures of tetrahedrally coordinated Cr\(^{4+}\) and Cr\(^{3+}\), respectively. The geometry of the cluster models is shown in Fig. 1. The coordinates of the atoms in the cluster were taken from the structure of the host YAG crystal, and the tetrahedrally coordinated Al atom at the center was replaced by a Cr atom. The symmetry at the Cr site is \(S_4\). Additional point charges with formal valences were placed at the atomic sites outside the cluster to reproduce the effective Madelung potential.

The calculated energy and transition probability of the \(3\)\(B\) state to the excited triplet states to the Lorentz resonance curve with a full width at half maximum of 325 cm\(^{-1}\). The peak energy and intensity ratio are compared with the experimentally obtained absorption spectrum in Fig. 2(b) taken from Ref. 1. In Fig. 2(a), we see that the \(3T_1\) multiplet term had a twofold splitting into the lower \(3\)\(A\) state and into the higher \(3\)\(E\) state due to the reduction of the symmetry from \(T_d\) to \(S_4\). The magnitude of the energy splitting was large at 5120 cm\(^{-1}\), and the splitting brought the two bands at the NIR and visible regions into the theoretical spectrum. This two-band structure agrees well with the structure in the experimental spectrum. We see from Table I that the calculated magnitude of the splitting also agreed with the experimentally deduced ones. 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 \(3\)\(B\) state to the excited triplet states.

The calculated energies of some excited states were compared with the experimentally obtained ground-state absorption spectrum taken from Ref. 1 for comparison.

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The calculated energies of the states located at the NIR region obtained from Cr\(^{4+}\) and Cr\(^{3+}\) 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 Cr\(^{5+}\) in the Cr\(^{4+}\)-doped system. Reinen \textit{et al.} studied diffuse reflectance spectra of Cr-doped Ca\(_3\)PO\(_4\)Cl and Ca\(_2\)(PO\(_4\))\(_3\)Cl, which had tetrahedrally coordinated sites. They revealed that the Cr\(^{5+}\)-like spectrum had specific bands in the 10 000–13 000 cm\(^{-1}\) region, which overlapped with the bands in the Cr\(^{4+}\)-like spectrum. Anino, Théry, and Vivien reported a band at 875 nm (11 430 cm\(^{-1}\)) in Cr-doped Li\(_2\)MgSiO\(_4\), and attributed the band to the \(2E\) transition of Cr\(^{5+}\). Our calculated energy of the

<table>
<thead>
<tr>
<th>States</th>
<th>This work</th>
<th>Eilers (1994)</th>
<th>Riley (1999)</th>
</tr>
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<tr>
<td>(3B(3T_1))</td>
<td>9 533</td>
<td>7 814</td>
<td>7 814, 7 842</td>
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<tr>
<td>(3E(3T_2))</td>
<td>10 490</td>
<td></td>
<td>~10 000</td>
</tr>
<tr>
<td>(3A(3T_1))</td>
<td>11 150</td>
<td>~10 000</td>
<td>8 977, 9 281</td>
</tr>
<tr>
<td>(3E(3T_2))</td>
<td>16 270</td>
<td>14 300–16 700</td>
<td>~15 000</td>
</tr>
<tr>
<td>(1B(1E))</td>
<td>6 805</td>
<td>8 264</td>
<td>~9 500</td>
</tr>
<tr>
<td>(1A(1E))</td>
<td>8 094</td>
<td>8 292</td>
<td>(Calc)</td>
</tr>
</tbody>
</table>

\(\text{Reference 1}\).

\(\text{Reference 10}\).
The authors investigated the relaxation of the Cr–O bond length estimated on the calculated multiplet energies by the simplest (CrO₄) cluster models, respectively. The magnitudes of the relaxation of the Cr–O bond length estimated by ionic radii were +1.1% for Cr⁴⁺ and −2.5% for Cr⁵⁺ based on the original Al–O bond length. The corresponding energy shifts were −240 cm⁻¹ for the ³B(3T₂) state of Cr⁴⁺ and +730 cm⁻¹ for the ²B(2T₂) state of Cr⁵⁺. 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. They attributed the zero-phonon lines to the ³B(3A₂) → ³B(3T₂) transition of Cr⁴⁺. 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) → ²B(2T₂) transition of Cr⁵⁺. There has been no study that discussed the existence of Cr⁵⁺ in Cr⁴⁺:YAG, although the existence had been already observed in garnet, Cr₃Ca₂Ga₂Ge₃O₁₂. We hope further experimental investigations will follow to reconfirm the assignment of the peaks in the absorption spectra of the Cr⁴⁺-doped system.

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