Multiplet structures of tetrahedrally coordinated Cr^{4+} and Cr^{5+} in $Y_3Al_5O_{12}$

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Multiplet structures of tetrahedrally coordinated Cr^{4+} and Cr^{5+} in $Y_3Al_5O_{12}$ (yttrium aluminum garnet) were calculated with use of the *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 *ab initio* calculation of multiplet structures of tetrahedrally coordinated Cr^{4+} and Cr^{5+} in $Y_3Al_5O_{12}$ [yttrium aluminum garnet (YAG)] crystal. First, we show that the revised assignment of the absorption spectrum proposed by Eilers *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 *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 *ab initio* methods. In Cr^{4+}:YAG, only a few studies have been done based on *ab initio* electronic-structure calculation methods. Sobolev *et al.* gave a simple discussion concerning the valence state of chromium by a cluster method.[4] Ching, Xu, and Brickeen conducted the band calculations, and proposed a model associated with excited-state absorption.[5] 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.[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_2GeO_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 *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

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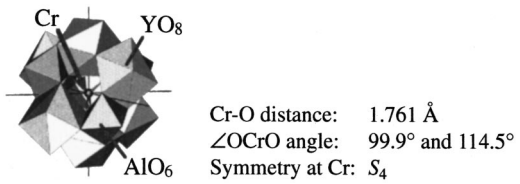

FIG. 1. Geometry of the ($CrY_6Al_4O_{44}$) cluster models. Additional point charges with formal valences are placed at the atomic sites outside the cluster to reproduce the effective Madelung potential.

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.[9] 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 $(CrY_6Al_4O_{44})^{54-}$ and $(CrY_6Al_4O_{44})^{53-}$ cluster models for calculation of the multiplet structures of tetrahedrally coordinated Cr^{4+} and Cr^{5+}, 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 four ligand O atoms around the Cr atom were completely shared by YO_8 and AlO_6 coordination polyhedra so that the covalency around the chromium was sufficiently described.

The calculated energy and transition probability of the Cr^{4+} states are shown in Fig. 2(a). The calculated levels are classified into singlet states (upper) and triplet states (lower). The symbols of the multiplet terms in the parent T_d symmetry and in the exact S_4 symmetry are attached to the levels. The calculated energies of some excited states were compared with the experimentally obtained peak energies described in the literatures,[1,10] summarized in Table I. The theoretical spectrum in the lower field in Fig. 2(a) was obtained by applying the calculated oscillator strength of the electric-dipole transition from the $^3B(^3A_2)$ 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 ^3A state and into the higher ^3E 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 $^3B(^3A_2)\rightarrow{}^3A(^3T_1)$ transition of the tetrahedrally coordinated 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.[10] 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.

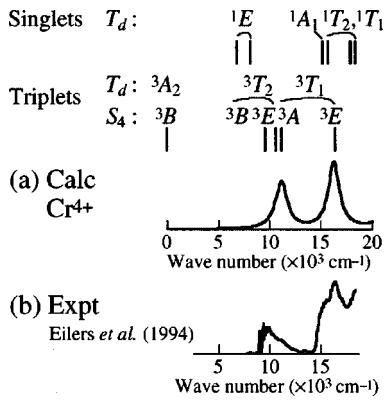

FIG. 2. Upper field in (a) the calculated peak energy obtained from the Cr^{4+} cluster model, classified into singlet and triplet states. Lower field in (a): theoretical absorption spectrum obtained by calculating the electric-dipole transition probability of the $^3B(^3A_2)\rightarrow$triplets transitions. (b) Experimentally obtained ground-state absorption spectrum taken from Ref. 1 for comparison.

TABLE I. Calculated and experimentally obtained energies (cm^{-1}) of the Cr^{4+} states.

States	This work	Eilers (1994)[a]	Riley (1999)[b]
$^3B(^3T_2)$	9 533	7 814	7814, 7 842
$^3E(^3T_2)$	10 490		≈10 000
$^3A(^3T_1)$	11 150	≈10 000	8977, 9 281
$^3E(^3T_1)$	16 270	14 300–16 700	≈15 000
$^1B(^1E)$	6 805	8 264	≈9 500
$^1A(^1E)$	8 094	8 292	(Calc)

[a]Reference 1.
[b]Reference 10.

The calculated energies of the states located at the NIR region obtained from Cr^{4+} and 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 Cr^{5+} in the Cr^{4+}-doped system. Reinen *et al.* studied diffuse reflectance spectra of Cr-doped Ca_2PO_4Cl and $Ca_5(PO_4)_3Cl$, 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.[11] Anino, Théry, and Vivien reported a band at 875 nm (11 430 cm^{-1}) in Cr-doped Li_2MgSiO_4, and attributed the band to the $^2E\rightarrow{}^2T_2$ transition of Cr^{5+}.[12] Our calculated energy of the

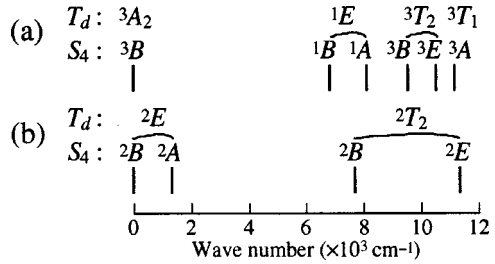

FIG. 3. (a) and (b) calculated energies of the states in the NIR region obtained from the Cr^{4+} and Cr^{5+} cluster models, respectively.

$^2E(^2T_2)$ state at 11 330 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 $^3B(^3A_2) \rightarrow {}^3A(^3T_1)$ transition of tetrahedrally coordinated Cr^{4+} and to the $^2B(^2E) \rightarrow {}^2E(^2T_2)$ 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^{5+}. Both states should be located below 10 000 cm^{-1} in the same energy region. Both the $^3B(^3A_2) \rightarrow {}^3B(^3T_2)$ and $^2B(^2E) \rightarrow {}^2B(^2T_2)$ 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 magnitudes 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 $^3B(^3A_2) \rightarrow {}^3B(^3T_2)$ 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 $^2B(^2E) \rightarrow {}^2B(^2T_2)$ transition of Cr^{5+}. 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, $Cr:Ca_3Ga_2Ge_3O_{12}$.[13] 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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