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Optical properties and electronic structures of layered MoO₃ single crystals

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Abstract

Reflectivity spectra of layered MoO₃ single crystals have been measured at 6 K in a wide energy range up to 25 eV. The spectra exhibit remarkable anisotropy for the polarization $E \parallel c$ and $E \parallel a$. Optical constants have been derived through the Kramers–Kronig analysis. The fundamental absorption tail located below 3.7 eV displays an exponential dependence on photon energy for both polarizations. It is found that two luminescence bands peaking at 2.93 and 3.58 eV are stimulated under the excitation with photons in the fundamental absorption region. Their decay behaviours are also examined at 8 K. With use of the discrete variational X α (DV X α) method, the electronic structure of an embedded [MoO₄] cluster has been calculated for better understanding of the optical properties of MoO₃. The calculated results are favourably compared with the experimental data.

1. Introduction

Molybdenum trioxide, MoO₃, is one of the transition metal oxides which have a number of technically important applications, e.g., electrochromism [1], photochromism [2] or catalysis [3]. The MoO₃ crystal has a very interesting orthorhombic layered structure with the space group D_{2h}¹⁶ (*Pbnm*) [4]. The structure of MoO₃ indeed represents a transitional stage between tetrahedral and octahedral coordination. As illustrated in figure 1, it may be considered as built up of chains of MoO₄ tetrahedra connected by the sharing of two oxygen corners with two neighbouring tetrahedra in the direction of the *c* axis. The infinite chains of MoO₄ tetrahedra form half-layers in the *ac* plane. Two half-layers, which are stapled along the *b* axis, build up one MoO₃ layer. When the two more distant oxygen atoms are included for one molybdenum atom, as indicated by dotted lines, the coordination can be regarded as sixfold, i.e., the layered structure consists of zig-zag rows of MoO₆ octahedra which share edges, while the rows are mutually connected by corners. The lattice constants are as follows: $a = 3.9628 \text{ \AA}$, $b = 13.855 \text{ \AA}$ and $c = 3.6964 \text{ \AA}$ [4].

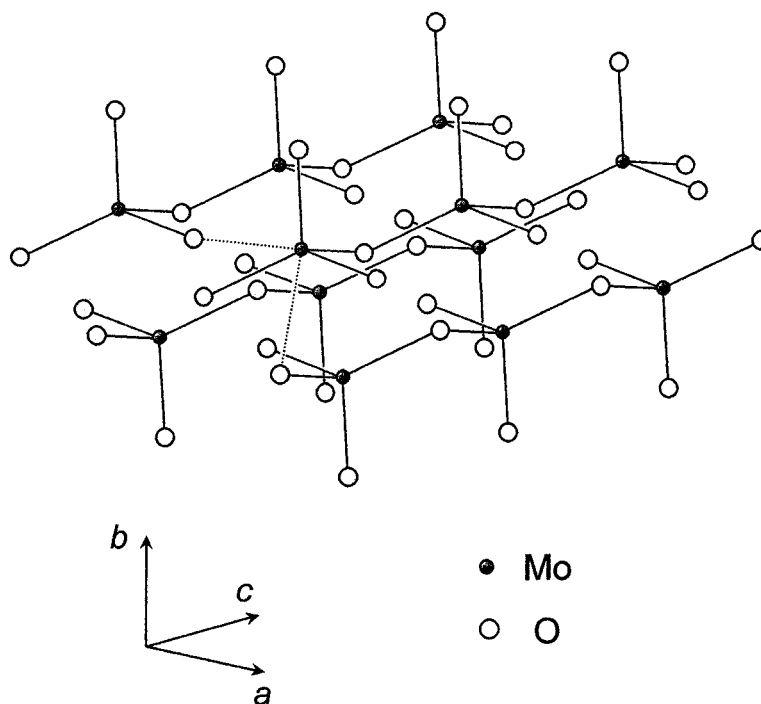


Figure 1. Crystal structure of MoO_3 visualized as built up of fourfold coordinated Mo atoms connected by O atoms to form chains parallel to the c axis. The dotted lines indicate for one Mo atom the two more distant O atoms. Only atoms in one bi-layer of the structure are shown.

Optical properties of amorphous or polycrystalline MoO_3 films have been intensively studied from the viewpoint of technology [1–3, 5–12]. On the other hand, few optical studies on single crystals of MoO_3 have been undertaken. Deb [6] has performed measurements of the fundamental absorption tail and the refractive index by using polarized light with the electric vector parallel to the c axis ($\mathbf{E} \parallel c$) and to the a axis ($\mathbf{E} \parallel a$). He has also measured the spectral distribution of photocurrent. The infrared and Raman spectra have been reported by Py and Maschke [13]. As far as we are aware, there has been no report on optical properties of MoO_3 crystals except for these two works. The basic optical spectra, such as reflectivity and luminescence, have not yet been investigated for this industrially important material.

In the present study, we have carried out a series of optical measurements on single crystals of molybdenum trioxide. The reflectivity spectra for the polarization $\mathbf{E} \parallel c$ and $\mathbf{E} \parallel a$ are measured at 6 K in the energy range up to 25 eV with the use of synchrotron radiation, and are transformed to the absorption spectra through a Kramers–Kronig analysis. The fundamental absorption tail is examined for $\mathbf{E} \parallel c$ and $\mathbf{E} \parallel a$ at various temperatures between 8 and 300 K. The luminescence spectra are investigated using polarized or unpolarized light as an exciting light source. The decay kinetics of luminescence is also measured under the irradiation by pulses from a laser. In addition, the electronic structure of MoO_3 is calculated by the discrete variational $X\alpha$ (DV $X\alpha$) method [14, 15]. We will discuss the optical properties of MoO_3 on the basis of these experimental and theoretical results.

2. Experiment

Single crystals of MoO₃ used in the present experiment were grown by the sublimation method. A silica crucible filled with reagent grade MoO₃ powder (5–10 g) was heated by an electric furnace at about 850 °C for 10 h. The temperature gradient along the crucible allowed the material to sublime and grow as thin crystals having sizes of up to 20 × 2 mm² and thicknesses of 0.3 mm. The resulting crystals were rectangular in shape, with a well developed *ac* plane, and were colourless and transparent. The crystal orientation was confirmed by the x-ray analysis. The specimen having a freshly cleaved *ac* surface was mounted on the copper holder in a variable-temperature cryostat.

Reflection measurements were carried out with the use of synchrotron radiation (SR) at beam line 1B of the UVSOR storage ring in the Institute for Molecular Science, Okazaki, as a light source. The SR was dispersed with a 1 m Seya-Namioka monochromator. The reflectivity spectra were measured under near-normal incidence configuration.

For the measurements of transmission spectra, visible light from a 500 W Xe lamp was dispersed with a Nikon G250 monochromator, and focused on the sample surface by a concave mirror ($f = 200$ mm). A Glan–Thompson polarizer or an ultraviolet polarizing filter was installed between the mirror and the sample. The transmitted light was detected by a photomultiplier tube (HPK, R106UH). For the measurements of luminescence and excitation spectra, the Xe lamp was replaced by a 150 W D₂ lamp to use ultraviolet light as an exciting light source. Luminescence from the sample surface was observed by means of a Jobin Yvon HR320 monochromator and a photomultiplier tube (HPK, R106UH or R955). The luminescence spectra reported here were corrected for the dispersion of the analysing monochromator and for the spectral response of the detection system. The excitation spectra were also corrected for the intensity distribution of the incident light.

We observed the decay behaviour of the luminescence features by using the fourth harmonic ($\hbar\omega = 4.66$ eV, pulse width = 5 ns) from a *Q*-switched Nd:YAG laser. The 4.66 eV photon falls well above the fundamental absorption edge of MoO₃. It is known [5, 6] that the MoO₃ crystal is decomposed by irradiation with intense light. Special care, therefore, should be taken on this point, when laser pulses are used to excite MoO₃ crystals. In this experiment, the sample was irradiated by an unfocused laser beam with energy fluxes less than 5 μJ mm⁻². The decay curves were recorded on a Tektronix 2440 digital storage oscilloscope operated in an averaging mode.

3. Experimental results

Figure 2 shows reflectivity spectra of MoO₃ crystals in the 3.5–25.0 eV region at 6 K for polarization $\mathbf{E} \parallel c$ and $\mathbf{E} \parallel a$. The absolute values of the reflectivity were not measured in our experiment. Fortunately, the refractive indices at 2.1 eV are known to be 2.54 for $\mathbf{E} \parallel c$ and 2.29 for $\mathbf{E} \parallel a$ [6]. Using these values, we obtained the reflectivity spectra of figure 2. The spectra exhibit remarkable polarization dependence. The strongest band for $\mathbf{E} \parallel c$ is seen at 4.5 eV, while that for $\mathbf{E} \parallel a$ appears at around 5.5 eV. Both spectra are structure rich in the energy region below 12 eV.

The real part ϵ_1 and imaginary part ϵ_2 of the dielectric functions for $\mathbf{E} \parallel c$ and $\mathbf{E} \parallel a$ have been derived through a Kramers–Kronig analysis of the reflectivity spectra in figure 2. The ϵ_1 and ϵ_2 spectra obtained are shown in figures 3(a) and 3(b), respectively.

The absorption spectra have also been obtained through the Kramers–Kronig transformation. The results are presented in figure 4, where the inset shows the spectra in the 3.5–7.0 eV region on an expanded scale. For $\mathbf{E} \parallel c$ (solid curve) three distinct bands are

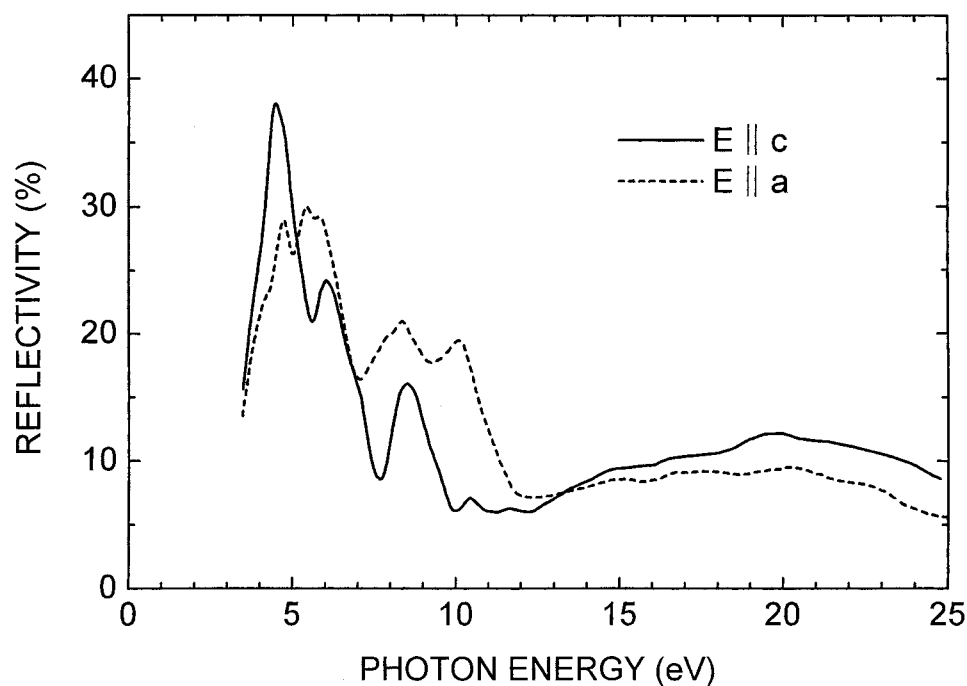


Figure 2. Reflectivity spectra of MoO₃ crystals at 6 K. The spectra were measured for the polarization $E \parallel c$ (solid curve) and $E \parallel a$ (broken curve).

observed at 4.7, 6.2 and 8.8 eV, and two weak peaks are seen at 10.5 and 11.8 eV. For $E \parallel a$ (broken curve) one can see a doublet structure peaking at 5.5 and 6.0 eV, with a shoulder-like structure at 4.8 eV. In addition, two intense bands appear at around 8.4 and 10.1 eV. A broad band with some weak structures is seen in the high-energy region above 13 eV for both polarizations.

Absorption spectra at the fundamental absorption edge of a MoO₃ crystal for $E \parallel c$ and $E \parallel a$ at 8 K are shown by solid and broken curves in figure 5, respectively. The thickness of the sample was 21 μm . Note that the absorption coefficient of figure 5 is 10^3 smaller than that of figure 4. The absorption edge is sensitive to the polarization vector of the incident light; the optical absorption for $E \parallel c$ rises at lower energy compared to that for $E \parallel a$. This polarization dependence of the absorption edge is in contrast to that of [6], but is consistent with our result (figure 4) that the absorption coefficient in the edge region is stronger for $E \parallel c$ than for $E \parallel a$. Additionally, the absorption spectra measured by Deb [6] exhibit three weak bands at 2.92, 3.00 and 3.15 eV. Similar bands, however, are not seen in figure 5. Since these absorption bands are likely ascribed to lattice imperfections, the present result indicates that the quality of our single crystals is better than that of his samples.

Deb [6] has pointed out that the low-energy tail of the fundamental absorption edge of MoO₃ crystals follows Urbach's rule [16]. In our measurements, too, the fundamental absorption tail located below 3.7 eV was found to increase exponentially with increasing photon energy at various temperatures between 78 and 300 K. That is, a logarithmic plot of the absorption coefficient could be fitted by a straight line over two orders of magnitude against photon energy. From the slope of the straight line at 300 K, we got the steepness parameter $\sigma = 0.20$ for $E \parallel c$ and 0.24 for $E \parallel a$. These values are roughly coincident with those (0.24 for $E \parallel c$ and 0.21 for $E \parallel a$) obtained by Deb.

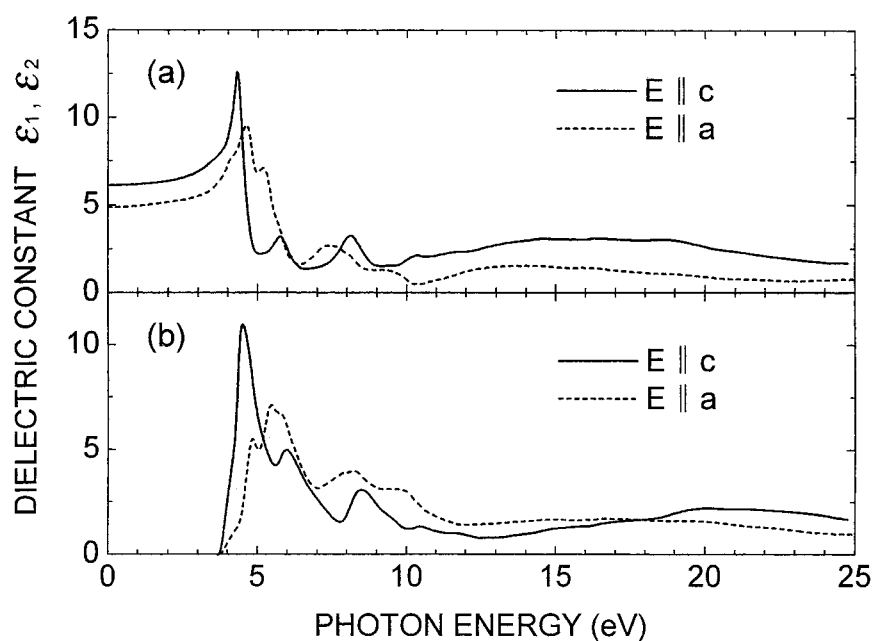


Figure 3. The real part ϵ_1 and imaginary part ϵ_2 of the dielectric function derived through the Kramers–Kronig analysis; (a) is for ϵ_1 and (b) is for ϵ_2 . The solid and broken curves correspond to $E \parallel c$ and $E \parallel a$, respectively.

It was found that luminescence spectra of MoO₃ crystals are insensitive to the polarization vector of the exciting light. In figure 6 is shown the luminescence spectrum observed under the excitation with unpolarized 5.39 eV light at 8 K. One can see two bands peaking at 2.93 and 3.58 eV. The 2.93 eV band is somewhat asymmetric in shape and tails to the low-energy side, with a full width at half maximum (FWHM) of 0.55 eV. The FWHM of the 3.58 eV band is about 0.35 eV. Both bands were thermally quenched in nearly the same way; their intensities decreased by more than a factor of 10 in warming from 8 to 300 K. The excitation spectra for the 2.93 and 3.58 eV luminescence bands observed at 8 K are also shown in figure 6. Both excitation spectra rise smoothly at the same energy (~ 3.8 eV), followed by two broad maxima at 4.5 and 5.5 eV. This excitation threshold coincides with the fundamental absorption edge of figure 4.

Decay behaviours of the 3.58 and 2.93 eV luminescence measured at 8 K are depicted in figure 7. The 3.58 eV luminescence decay consists of two exponential components. Since the fast component decays on the time scale of the laser-pulse duration, analysis of the decay curve requires treatment of convolution integrals. From this analysis, we get a fast decay time 2.5 ± 1.0 ns and a slow decay time 47 ± 5 ns. The time-integrated intensity of the fast component is nearly equal to that of the slow component. The decay curve of the 2.93 eV luminescence is reproduced by the convolution integral including just a single exponential function. The decay time obtained is 5.0 ± 1.0 ns. After the laser irradiation, the sample surface was examined by the eye or using an optical microscope. No symptoms of photochemical decomposition and coloration were observed.

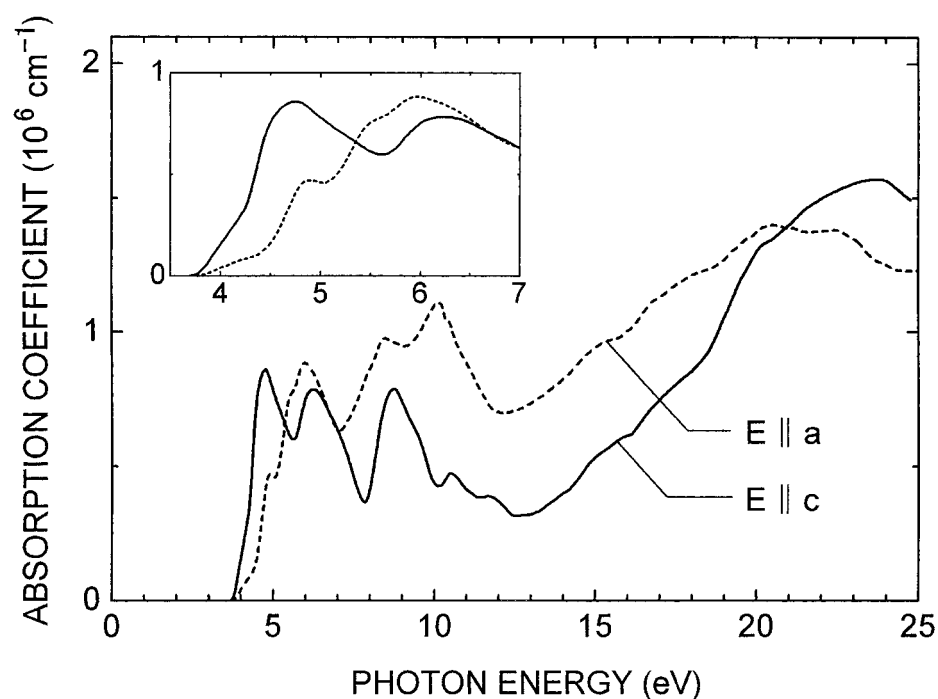


Figure 4. Absorption spectra of MoO₃ for $E \parallel c$ (solid curve) and $E \parallel a$ (broken curve) at 6 K. The inset shows the absorption spectra in the 3.5–7.0 eV region on an expanded scale.

4. Electronic structures by the DV X α calculation

No electronic band calculation on MoO₃ is available in the literature. We therefore calculated the electronic states of model clusters of MoO₃ by using the DV X α method, which has been successfully applied to various types of inorganic compound. The computational details of this method have been described in [15]. The basis functions included in the calculation were 1s to 5p atomic orbitals for the molybdenum ion and 1s to 2p atomic orbitals for the oxygen ion. The interatomic distances were taken from the experimental data of the crystal [4].

In the case of cluster calculation for ionic compounds, some of the molecular orbitals localized on the surface atoms in the cluster are often affected by electrostatic potentials due to the ions surrounding the cluster. Because of the low symmetry of MoO₃ and also of the transitional character between octahedral and tetrahedral coordination, we first investigated two simple clusters, [MoO₆] and [MoO₄], without taking account of the influence of electrostatic potentials due to the ions outside the cluster. The calculations for these two clusters led to similar electronic structures; i.e., the bottom of the conduction band is mainly built up of the 4d state of molybdenum ions, and the top of the valence band is dominated by the 2p state of oxygen ions. The two clusters, however, differed in the band-gap energy; 0.56 eV for [MoO₆] and 3.22 eV for [MoO₄]. The former is too small, while the latter is reasonable in comparison with the experimental data.

Based on the results mentioned above, we further investigated an embedded [MoO₄] cluster model in order to get a more reliable result. In this model, the [MoO₄] cluster is properly surrounded by point charges located at the external atomic sites. These point charges stabilize the cluster by reducing the influence of electrostatic potentials due to the ions outside

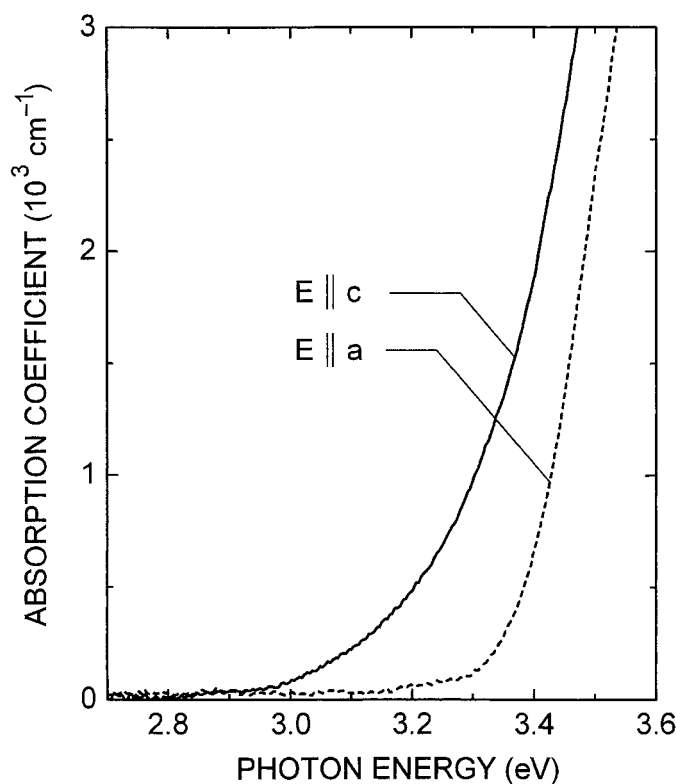


Figure 5. Fundamental absorption tails of MoO₃ for $E \parallel c$ (solid curve) and $E \parallel a$ (broken curve) at 8 K. The thickness of the sample was 21 μm .

the cluster. As shown by the inset in figure 8, the four oxygen ions tetrahedrally arranged around the central molybdenum ion in [MoO₄] cluster are represented as O(I), O(II) and O(III). The O(I)–Mo–O(I) bridge is parallel to the c axis.

The electronic structure obtained for the embedded [MoO₄] cluster is shown in figure 8, where the energy is referred to the top of the valence band. The total energy levels are indicated on the left side. Solid and broken lines represent occupied and unoccupied levels, respectively. The length of a line of each state indicates the partial contribution to the corresponding total one. It appears that the top of the valence band is composed of the 2p state of O(I), with small contributions from O(II) and O(III). The 2p states of O(II) and O(III) are located at -1.79 eV below the top of the valence band. The lowest valence band is mainly formed from the O(II) 2p state. The valence-band width is estimated to be 6.98 eV. The O 2s core level lies at around -17.5 eV. On the other hand, the lowest conduction band is constructed by the Mo 4d state, which somewhat hybridizes with the 2p state of the four oxygen neighbours. The higher-lying 5s and 5p states of molybdenum ions are situated at 13.6 eV and at 18.0 and 20.0 eV, respectively. The calculated band-gap energy is 3.87 eV.

5. Discussion

In a number of ionic compounds [17] and also in layered structures such as MoS₂ [18], a sharp isolated peak due to excitonic transition has been observed at the fundamental absorption edge.

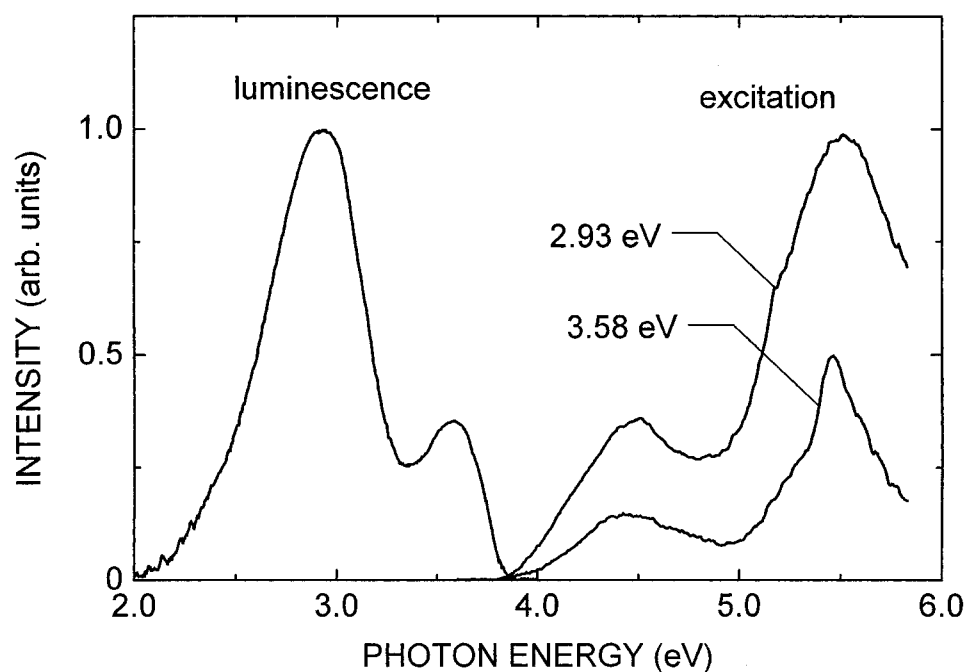


Figure 6. Luminescence spectrum of MoO₃ excited with unpolarized 5.39 eV light at 8 K. Excitation spectra for the 2.93 and 3.58 eV luminescence bands are also shown.

At first glance, such a peak is not found in figure 4. One possible situation is that the binding energy of the exciton is too small to observe it as an isolated peak. Another situation is that the oscillator strength for the excitonic transition is small. If we look at the inset of figure 4 carefully, a small hump can be recognized at around 4.05 eV for $E \parallel c$ and $E \parallel a$. This structure may be assigned to the exciton transition. If this is the case, the two situations above are both supposed to hold for the excitons in MoO₃. On the basis of this assignment, the band-gap energy is estimated to be about 4.1 eV, leading to the exciton binding-energy of 50 meV or less. The present value of 4.1 eV for the band-gap energy is larger than 3.56 eV obtained from the photoconductivity measurements by Deb [6].

It is to be noted that no phonon structure due to indirect transition is seen at the fundamental absorption edge in figure 5. Accordingly, the minimum band gap of MoO₃ is considered to be of direct-allowed type. The present electronic structure calculation of MoO₃ indicates that the uppermost valence band is built up of the 2p state of oxygen ions, and the lowest conduction band is dominated by the 4d state of molybdenum ions. The same energy-level diagram has been proposed by Deb and Chopoorian [5]. The O 2p \rightarrow Mo 4d transition is indeed of allowed type. We calculated the band-gap energy to be 3.87 eV, which is in satisfactory agreement with our experimental value (\sim 4.1 eV).

In figure 4, the absorption spectra for both polarizations show a clear dip at 7–8 eV higher than the fundamental absorption edge. Since the valence-band width is calculated to be 6.98 eV, the structures below the dip may be attributed to the transitions from the valence band to the bottom of the conduction band. According to the electronic structure of figure 8, the top of the valence band is mainly composed of the 2p state of O(I), while the 2p states of O(II) and O(III) are located at -1.79 eV below the top of the valence band. When the incident angle is normal to the ac plane, the light with the electric vector parallel to the c axis will interact more

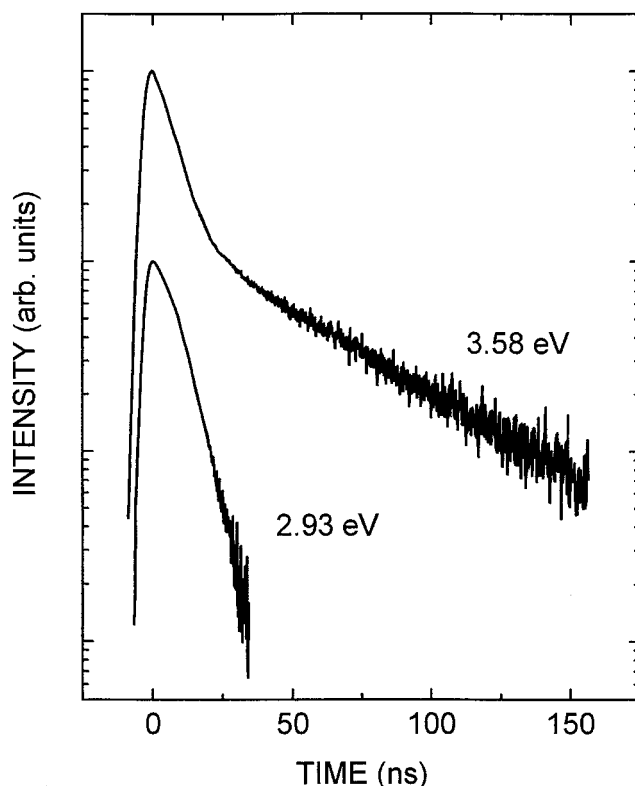


Figure 7. Decay profiles of the 3.58 and 2.93 eV luminescence in MoO₃. Each curve is vertically displaced for clarity. The excitation was made at 8 K with 4.66 eV photon pulses from a *Q*-switched Nd:YAG laser.

strongly with the Mo–O(I) bond than with the Mo–O(II) bond, and vice versa for the light with the electric vector parallel to the *a* axis. The present calculation can, therefore, explain the polarization dependence of the absorption spectra. Namely, the absorption spectrum for $E \parallel c$ shows an intense band at 4.7 eV, while that for $E \parallel a$ shows a remarkable structure around 6.0 eV. An absorption band at 10.1 eV is stronger for $E \parallel a$ than for $E \parallel c$. This fact is also consistent with the calculation that the lowest valence band is mainly formed by the O(II) 2p state.

The broad band, with some structures, above the dip would be ascribed to the transitions from the valence band to the high-lying Mo 5s and 5p states in the conduction band. For example, a weak peak observed at 11.8 eV in the $E \parallel c$ spectrum is probably assigned to an electronic transition from the top of the valence band formed by the O(I) 2p state to the Mo 5s state. The O 2s \rightarrow Mo 4d transition will also contribute to this broad band peaking between 20 and 24 eV.

The MoO₃ crystals exhibit two luminescence bands at 2.93 and 3.58 eV. This result is very different from that of amorphous MoO₃ films [10], in which only one broad luminescence band is observed at 1.65 eV. The 3.58 eV band is located close to the fundamental absorption edge; in other words, its Stokes shift is small. On the other hand, the 2.93 eV band has a relatively large Stokes shift. These two bands are stimulated with photons of an energy equal to or exceeding the exciton absorption, as shown in figure 6. Such a result suggests

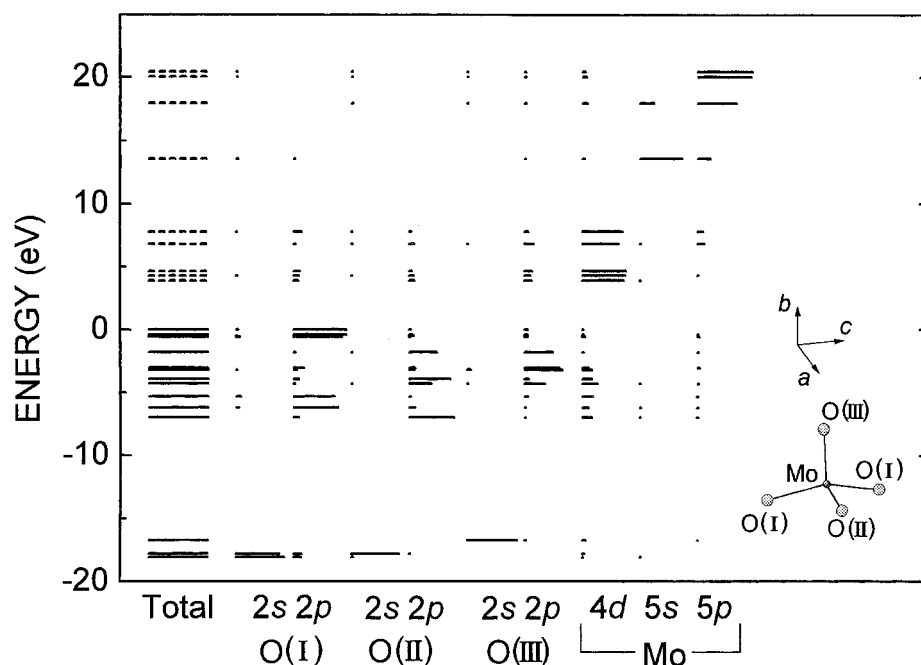


Figure 8. Electronic structure of the embedded $[\text{MoO}_4]$ cluster calculated by the DV $X\alpha$ method. The energy is referred to the top of the valence band. Solid and broken lines represent occupied and unoccupied levels, respectively. The inset shows the $[\text{MoO}_4]$ cluster with four oxygen ions indicated as O(I), O(II) and O(III), where the embedding point charges are not depicted.

the intrinsic nature of both luminescence bands, but does not rule out the possibility that photogenerated excitons or electron-hole pairs move about freely through the crystal and are trapped by some lattice imperfection from which the luminescence is emitted. Therefore, there are four possible speculations. (i) The 2.93 and 3.58 eV luminescence bands are both ascribed to radiative decay of a self-trapped exciton (STE). The excitons in MoO_3 are self-trapped by inducing two different types of lattice relaxation. One is a shallowly relaxed configuration that is responsible for the 3.58 eV luminescence. The other is a deeply relaxed one for the 2.93 eV luminescence. Among O(I), O(II) and O(III), the hole party to an exciton is expected to localize largely at the site of O(I), because it forms the uppermost valence band. The length and angle of the Mo-O(I)-Mo bond along with its immediate surroundings might be deformed when the exciton relaxes into the STE state. The details of such shallowly and deeply relaxed lattice configurations are not clear at present. (ii) The 3.58 eV luminescence is an extrinsic feature of MoO_3 , and arises from the radiative recombination of excitons localized at or near lattice imperfections. A plausible candidate for the lattice imperfection is an oxygen vacancy which is introduced as a result of the non-stoichiometry in MoO_3 crystals or is produced by the irradiation with ultraviolet light [6]. On the other hand, the 2.93 eV luminescence is attributed to the radiative recombination of STEs. (iii) The situation is the reverse of the case (ii). (iv) Both the 2.93 and 3.58 eV luminescence are linked to lattice imperfections. This requires two kinds of imperfection; for instance, one is a simple oxygen vacancy, and the other is a more complex defect centre, such as the clustering of oxygen vacancies or the lower valence Mo^{5+} ion associated with an oxygen vacancy as neighbour.

In MoO₃, the steepness parameters are 0.20 and 0.24 for $E \parallel c$ and $E \parallel a$, respectively. According to the theoretical approach by Sumi and Toyozawa [19], the steepness parameter σ is inversely proportional to the strength of the exciton–phonon interaction. When σ is smaller than the critical value σ_c , an exciton becomes self-trapped, giving rise to a Stokes-shifted broad luminescence band. When σ exceeds σ_c , the self-trapping of excitons does not take place, and free-exciton luminescence is observable. The values of σ_c have been estimated to be 1.24 for two-dimensional lattices and 1.50 for three-dimensional lattices [20]. Since MoO₃ is a layer-type compound, its properties are expected to be somewhere between two and three dimensions. The present values of σ are significantly smaller than 1.24 and 1.50, which suggests a strong coupling of the exciton–phonon interaction in MoO₃. These arguments are not favourable for the speculations (i) and (iii) described above. We suppose that case (ii) is the most plausible interpretation.

The excitons are self-trapped or localized as a result of successive scattering by phonons. Therefore, the polarization memory of the exciting light will be lost during the self-trapping or localization process of the excitons. This explains the fact that the luminescence spectra observed for the exciting light with $E \parallel c$ and $E \parallel a$ are not different from each other.

The exciton state is split into a singlet–triplet mixed state and a pure triplet state, if the exchange interaction between electron and hole is taken into account [21]. The former is dipole active for the electric-dipole transitions, and the latter is spin forbidden. Because of the low symmetry of MoO₃, the crystal-field splitting may also play an important role in lifting the degeneracy of the emitting state. The 2.93 and 3.58 eV luminescence bands have fast decay times of the order of a nanosecond. Therefore, it can be thought that the singlet states are responsible for both bands. A relatively slow decay component of the 3.58 eV luminescence may be ascribed to the radiative transition from the triplet state, which is partially allowed owing to the spin–orbit coupling with higher singlet states.

It is noteworthy that the fast exponential decay curves observed here clearly exclude the possibility that the 2.93 and 3.58 eV luminescence originate from radiative tunnelling recombination between a trapped hole and a trapped electron. This kind of tunnelling luminescence is characterized by a decay curve which is proportional to $(\text{time})^{-1}$, and has often been observed in semiconductors [22] and insulators [23].

6. Summary

To our knowledge, this paper is the first report on the reflectivity and luminescence spectra of single crystals of molybdenum trioxide. We measured the polarized reflectivity spectra in the 3–25 eV range. The optical constants were derived through the Kramers–Kronig transformation. The electronic structure of an embedded [MoO₄] cluster was also calculated by the DV X α method. The calculated result explained well the experimental data. We found two luminescence bands with lifetime of the order of a nanosecond; one is situated near the fundamental absorption edge and the other is greatly Stokes shifted. Their origins were discussed in connection with the strength of the exciton–phonon interaction, although further investigation is necessary to make them certain.

Acknowledgments

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