A Comparative Study of the Electronic Spectra of Bisperiodato-Cuprates(II,III), Y_2BaCuO_5, and $YBa_2Cu_3O_{7-\delta}$ (δ = 0, 1)

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The electronic spectra of bisperiodato-cuprates (II,III), Y_2BaCuO_5, and thin films of $YBa_2Cu_3O_{7-\delta}$ have been investigated between 0.5 and 5 eV by diffuse reflectance or transmittance spectroscopy. The periodato-complexes are used to establish the spectral characteristics of divalent and trivalent copper in an oxygen atom environment. Comparison of the spectra of the Cu(II) complex with those of Y_2BaCuO_5 and $YBa_2Cu_3O_6$ indicates that several features in the visible part of the spectra in all these compounds correspond to "d–d" transitions typical for divalent copper. In $YBa_2Cu_3O_6$ divalent copper is located only in the Cu(2)-oxygen planes since crystal chemistry requires the Cu(1) atoms to be monovalent. The spectra for metallic $YBa_2Cu_3O_7$ are completely different from those of $YBa_2Cu_3O_6$ indicating that at least in the Cu–O planes no individual valences of the copper atoms can be distinguished. The optical response of the Cu(1) atom in $YBa_2Cu_3O_7$ is not yet clear. Comparison of the spectra of $YBa_2Cu_3O_7$ with those of the Cu(III) complex, however, shows that the presence of trivalent copper cannot be excluded. © 1990 Academic Press, Inc.

1. Introduction

In order to make progress in understanding the pairing mechanism which leads to superconductivity in the perovskite-based metal oxides a detailed knowledge of their electronic properties is required. With the exception of $K_xBa_{1-x}BiO_3$ (*1, 2*) the new high T_c materials contain the transition metal copper. The study of the electronic properties of these compounds has been discussed extensively (*3*). Problems in this field include the extent of localization and mixing of the electronic states and the valence state of the central ion. $YBa_2Cu_3O_6$, e.g., is a semiconductor, and $YBa_2Cu_3O_7$ shows metallic behavior and superconductivity below 90 K. Simple one-elec-

tron band theory would predict metallic behavior in both cases because the partially filled $3d$ orbitals should give rise to partially filled conduction bands. On the other hand the correlation energy reflecting the Coulomb repulsion between the d electrons at the same site may suppress conductivity (*4*) as in the classic example NiO, which, in spite of its only partially occupied d shell, is an insulator (*5*). In this context the question about the valence states of copper in $YBa_2Cu_3O_{7-\delta}$ arises.

Starting from an oxidation state -2 for oxygen in $YBa_2Cu_3O_{7-\delta}$ one calculates the Cu oxidation states 1.67 for δ = 1 and 2.33 for δ = 0, respectively, which suggests the presence of monovalent copper in the former and trivalent copper in the latter

case. This picture is supported by the crystal chemistry of the materials. Both, the tetragonal ($\delta = 1$) and the orthorhombic ($\delta = 0$) phase, contain copper in two crystallographically distinct sites. At the Cu(2) sites copper is in a square pyramidal environment of oxygen atoms with a mean equatorial copper–oxygen distance d_{Cu-O} of 1.94 Å typical for divalent copper. In $YBa_2Cu_3O_6$ the distance between the Cu(2) atom and the apical O(1) atom (2.47 Å) is about 0.17 Å larger than in $YBa_2Cu_3O_7$ (6). The Cu(1) atom is coordinated linearly by two O(1) atoms with $d_{Cu-O} = 1.80$ Å in $YBa_2Cu_3O_6$. The short bond length as well as the linear coordination are typical for monovalent copper. In $YBa_2Cu_3O_7$ the additional oxygen gives rise to the formation of Cu(1)–O(4) chains with $d_{Cu-O} = 1.94$ Å, yielding a rectangular coordination for copper. The short Cu(1)–O(1) bondlength (1.85 Å) in connection with the fourfold coordination of copper led to the assumption that the Cu(III) expected from stoichiometry is mainly located at the Cu(1) sites (7, 8). Most of the spectroscopic studies, however, were not able to confirm the presence of Cu(III). Instead, holes in the oxygen band were found (9) suggesting that the O^{2-} anion is unstable in the presence of Cu(III), although some studies (e.g., by XPS) revealed some Cu(III) (10, 11).

Besides photoemission experiments (3), optical spectroscopy in the near IR, Vis, and near UV region is especially well suited to investigate the nature of valence electrons. Several studies applying reflectivity and ellipsometric measurements on ceramic samples as well as on single crystals of $YBa_2Cu_3O_{7-\delta}$ (12–15) have been performed. Also transmittance spectra of thin films of $YBa_2Cu_3O_{7-\delta}$ deposited on sapphire substrates were obtained (16, 17). From all these studies it is clear that drastic spectral changes occur when going from $\delta = 1$ to 0. The origin of the absorption peaks in the two phases, however, is still a matter of controversy.

Further insights into the nature of the transitions giving rise to these spectral features can be obtained from investigations of discrete oxocuprate complexes. In order to point out the spectral characteristics of divalent and trivalent copper we investigated the diffuse reflectance spectra of bisperiodato-cuprates(II,III). The optical spectra of the Cu(III) complex $Na_5[Cu(HIO_6)_2]$ have already been studied in solution (18). We also prepared a similar Cu(II) and a mixed-valent Cu(II,III) complex which are, however, not water-soluble and hence the solid state spectra are reported. In addition we measured the diffuse reflectance spectra of Y_2BaCuO_5 and the transmittance spectra of thin films of $YBa_2Cu_3O_{7-\delta}$ ($\delta = 0$, 1) on MgO substrates. The so-called "green phase" Y_2BaCuO_5 contains distorted copper–oxygen square pyramids which are not connected directly via oxygen bridges (19). Thus Y_2BaCuO_5 might serve as a link between the "molecular" complexes and the two-dimensional copper–oxygen planes in the superconductors. The spectra of $YBa_2Cu_3O_{7-\delta}$ will be analyzed especially with respect to the question of whether there is evidence for rather localized d electrons which reflect the valence states of the copper atoms.

2. Experimental

2.1 Synthesis of the Materials

Sodium bisperiodato-cuprate(III). The copper(III) complex $Na_5[Cu(HIO_6)_2]$ * $12H_2O$ was prepared from $NaIO_4$ and $CuSO_4$ * $5H_2O$ in alkaline solution with $K_2S_2O_8$ as an oxidizing agent according to Ref. (20). The compound was obtained as a dark brown polycrystalline material.

Sodium bisperiodato-cuprate(II). The bisperiodato-cuprate(II) was obtained in a similar way as the complex with trivalent copper but without oxidizing agent. $NaIO_4$ (2.14 g; 0.01 mole) and KOH (6 g) were dissolved in 100 ml water. $CuSO_4$ * $5H_2O$ (1.25 g; 0.005 mole) dissolved in 30 ml water were added dropwise under stirring at room tem-

perature. A deep blue solution with a certain amount of a solid precepitate was obtained. The solution was filtered and an aqueous solution containing 6 g $NaNO_3$ was added. After some time a fine blue precipitate appeared which was collected after keeping overnight. The resulting powder was washed several times with water and dried *in vacuo* over CaO. In contrast to the copper(III) complex the copper(II) complex is not soluble in water.

Mixed-valent sodium bisperiodato-cuprate(II,III). The complex was prepared in the presence of $K_2S_2O_8$ as an oxidizing agent in a similar way as the copper(III) complex but only half of the amount $K_2S_2O_8$ necessary for complete oxidation to Cu(III) was used. $NaIO_4$ (2.7 g; 0012 mole), $K_2S_2O_8$ (0.45 g; 0.002 mole), and KOH (8 g) were dissolved in 100 ml water. An aqueous solution of $CuSO_4 * 5H_2O$ (1.6 g; 0.006 mole) was added. The solution was stirred at room temperature for 3 hr. The color of the solution changed from blue via green to brownish green. After filtrating and adding an aqueous solution of 7.5 g $NaNO_3$ a green powder was obtained which was washed several times with water and dried *in vacuo* over CaO. The filtrate has an intense brown color indicating the presence of the pure copper(III) complex in solution.

Some chemical evidence that the green complex indeed contains copper in the valence states II and III is obtained from the fact that addition of the reducing agent $Na_2S_2O_3$ to an alkaline suspension of the green complex results in the formation of the blue complex. Furthermore, starting from the brown solution of $Na_5[Cu(HIO_6)_2]$ and adding $Na_2S_2O_3$ the color changes from brown via green to blue.

Y_2BaCuO_5. The compound was prepared via the usual solid state reaction (21).

Characterization of the compounds. The Guinier diagrams of $Na_5[Cu(HIO_6)_2]$ * $12H_2O$ and Y_2BaCuO_5 were in agreement with the powder patterns calculated from

the structures (19, 22). The divalent (blue) and mixed-valent (green) bisperiodato-cuprates were poorly crystallized and gave only weak reflections. Their powder diagrams were found to be identical to each other, but different from that of Na_5 $[Cu(HIO_6)_2]$ * $12H_2O$. Elemental analysis for Na, K, Cu, and I was performed by AES-ICP and led to ratios I : Cu : Na : K of 2 : 1.2 : 5.5 : 0.3 for the blue complex and 2 : 1.1 : 5.4 : 0.2 for the green complex, respectively. The amount of crystal water was not determined. If the small content of K is neglected the ideal composition $Na_6[Cu(HIO_6)_2]$ * yH_2O is derived for the blue complex. The somewhat smaller cation content indicates the presence of Cu(III) in the green complex.

Thin films of $YBa_2Cu_3O_{7-\delta}$. Thin films of $YBa_2Cu_3O_{7-\delta}$ were prepared by means of the pulsed laser deposition technique (23) combined with *in situ* crystallization and oxidation. The substrate was a (100)-oriented MgO single crystal. Using a substrate temperature of 780°C and an oxygen background pressure of 10^2 Pa films grew in the tetragonal phase and converted to the superconducting orthorhombic phase during cooling in air. In order to prevent any contamination of the substrate prior to deposition of the first layer a special heating system was developed which allows a clamp-free mounting and radiative heating of the substrate in a quartz crucible (24). The films with a thickness of approximately 1500 Å were single phase YBa_2 $Cu_3O_{7-\delta}$ material with the c-axis perpendicular to the substrate surface as revealed by X-ray diffractometry. The transition to superconductivity is characterized by a zero resistance at 88 K and a transition width of 0.5 K (90–10% transition). Thin films of the tetragonal $YBa_2Cu_3O_6$ phase were prepared by extracting oxygen from the orthorhombic phase by a 2-hr treatment *in vacuo* at 500°C. The extraction of oxygen from the YBa_2 $Cu_3O_{7-\delta}$ film is associated with an increase of the c-axis from 11.68 to 11.83 Å as derived

from the X-ray data. Comparison with liter-
ature data (6, 25) shows $\delta \leq 0.1$ for the
superconducting film and $\delta \approx 1$ for the semi-
conducting film, respectively.

2.2 Optical Spectroscopy

Diffuse reflectance spectra of the com-
plexes and Y_2BaCuO_5 as well as transmit-
tance spectra of thin films of $YBa_2Cu_3O_{7-\delta}$
on MgO between 0.5 and 5 eV were obtained
with a Perkin–Elmer Lambda 9 double beam
spectrometer. In addition transmittance
spectra of an aqueous solution of Na_5
$[Cu(HIO_6)_2]$ were recorded. For the diffuse
reflectance spectra the spectrometer was
equipped with a 60-mm integrating sphere at-
tachment which is internally coated with
$BaSO_4$. The powder samples were finely
ground in an agate mortar in order to obtain
small particle sizes and to minimize the ef-
fects of specular reflectance (26). In the range
of intense absorption, however, the spectra
are expected to be flattened. A better resolu-
tion of the structures in this range was
achieved by diluting the compounds with
$BaSO_4$ (Bariumsulfat für Weissstandard
DIN 5033, Fa. Merck). For this purpose mix-
tures with a molar fraction of the sample
of ca. $2 \cdot 10^{-3}$ were ground for 10 hr in a ball
mill. As a reference, pure $BaSO_4$ treated in
the same manner was used. A MgO substrate
exposed to the same thermal treatment as
the substrate containing the thin films was
used as a reference for the transmittance
spectra of $YBa_2Cu_3O_{7-\delta}$ films. The spectra
are displayed as the logarithm $\log(1/R)$ of the
inverse reflectance in the case of reflectance
spectra and as the logarithm $\log(1/T)$ of the
inverse transmittance in the case of transmit-
tance spectra.

3. Experimental Results and Discussion

3.1 Bisperiodato-Cuprates(II,III)

In Fig. 1 the diffuse reflectance spectra of
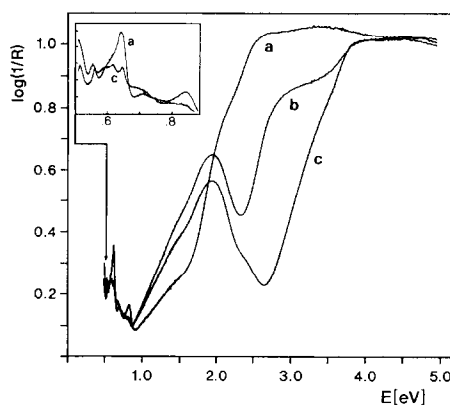the three complexes in the range from 0.5 to

FIG. 1. Diffuse reflectance spectra of powders of
bisperiodato-cuprate complexes, (a) $Na_5[Cu(HIO_6)_2]$
* $12H_2O$ (Cu(III)), (b) $Na_{6-x}[Cu(HIO_6)_2]$ * yH_2O
(Cu(II,III)), (c) $Na_6[Cu(HIO_6)_2]$ * yH_2O (Cu(II)).
Inset: Near IR spectra of the Cu(III) (a) and the
Cu(II)(c) complex.

5 eV are shown. The spectra of the blue
Cu(II) complex are characterized by two
well-separated areas of absorption. A broad
low energy band with a maximum at 1.9 eV
has shoulders at 1.5 and 2.4 eV. It is less
intense than the high energy absorption
around 4 eV. In contrast the spectra of the
brown Cu(III) complex reveal intense ab-
sorption over the whole spectral range
above 2 eV. In Fig. 2 the spectra of
the Cu(II) and Cu(III) complexes diluted
with $BaSO_4$ together with the spectrum of
$Na_5[Cu(HIO_6)_2]$ in aqueous solution are
given. Again for the Cu(II) complex a broad
band of lower intensity extending from 0.9
to 2.4 eV is found. The structures seen in
the spectra of the undiluted complexes are
not resolved. In contrast to the Cu(II) com-
plex which has an absorption minimum
around 2.5 eV, a broad intense absorption
band around 2.8 eV with a shoulder at 2.2
eV appears for the Cu(III) complex. The
great intensity of the 2.8 eV band is evidence
that it is due to a dipole-allowed transition.
Both complexes reveal intense absorption
around 4.1 eV at almost the same position

which therefore most probably is due to an intraligand transition. The structure of the high energy part of the diffuse reflectance spectrum of $Na_5[Cu(HIO_6)_2] * 12H_2O$ compares well with that of the transmittance spectrum of an aqueous solution of the complex although the line positions are shifted by a certain amount. Positions and intensities of the bands at 2.9 eV (ε_{max} = 10,660 mole^{-1} liter^{-1} cm) and 4.7 eV (ε_{max} = 11,070 mole^{-1} liter^{-1} cm) in the solution spectra are in good agreement with those reported in literature (18). In addition we found an intense band at 5.9 eV with ε_{max} = 19,600 mole^{-1} liter^{-1} cm (not shown in Fig. 2). Even in more concentrated solutions there are no absorptions between 1.2 and 2 eV in the spectra. It is therefore concluded that no absorptions below 2 eV are intrinsic for the Cu(III) complex. In contrast some intensity below 2 eV is found in the reflectance spectra of the Cu(III) complex. It is likely that this feature is due to a certain amount of Cu(II) which is more easily seen in the reflectance spectra than in the transmittance
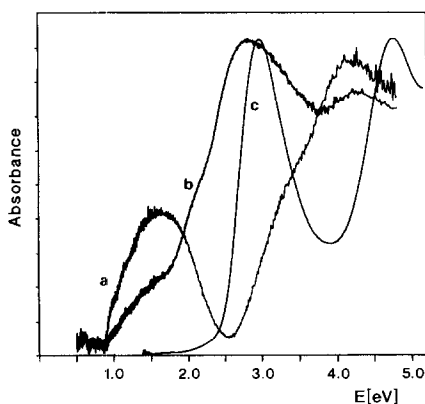

FIG. 2. Diffuse reflectance spectra of (a) sodium bisperiodato-cuprate(II) diluted with $BaSO_4$. (b) Sodium bisperiodato-cuprate(III) diluted with $BaSO_4$. (c) Transmittance spectrum of an aqueous solution of Na_5 [$Cu(HIO_6)_2$], $c = 5 \cdot 10^{-5}$ mole liter^{-1}, optical path length $d = 0.5$ cm. The spectra are given in an arbitrary scale.

spectra of solutions. Several absorptions due to overtone vibrations of the crystal water occur in the near IR spectra of the undiluted complexes. In the spectra of the Cu(III) complex, however, an additional absorption of low intensity at 0.64 eV (Fig. 1 inset) with a halfwidth less than 0.05 eV seems to be superimposed to the absorptions of the crystal water.

The differences in the electronic spectra of the complexes with Cu(II) and Cu(III) can be well understood by the different electronic transitions arising from the d^9 and d^8 configurations, respectively. In the crystal structure of the Cu(III) complex $Na_5[Cu(HIO_6)_2] * 12H_2O$ the copper atom is surrounded by four oxygen atoms with Cu–O distances between 1.81 and 1.86 Å (22). The Cu–O distances of two additional oxygen atoms of crystal water (2.7 and 3.6 Å, respectively) are much longer. The following approximate analysis of the spectra will be based on the assumption of D_{4h} symmetry of the ligand field. The coordinate system throughout the paper will be chosen so that the equatorial ligand atoms are located along the x and y axes, and the apical ligand atoms along the z axis, respectively. In this case the five d orbitals are split into $e_g(xz, yz)$, $b_{2g}(xy)$, $a_{1g}(z^2)$, and $b_{1g}(x^2 - y^2)$ orbitals. It is expected that the $x^2 - y^2$ orbital is highest in energy. As the real symmetry is lower than D_{4h} also the degeneracy of the e_g orbitals may be removed. For the Cu(II) complex three "d–d" transitions (four in the case of lower symmetry) into the $x^2 - y^2$ orbital should occur ($^2B_{1g} \rightarrow {}^2B_{2g}$, $^2B_{1g} \rightarrow {}^2A_{1g}$, $^2B_{1g} \rightarrow {}^2E_g$). Since the "$d$–$d$" transitions are parity-forbidden their intensity is lower than the intensity of (spin-allowed) charge transfer transitions. Thus the broad band near 2 eV in the spectra of the Cu(II) complex, the structure of which (Fig. 1) indicates that at least three transitions are involved, is assigned to the superposition of the different "d–d" transitions. Energy range and splitting of this band are similar to

other Cu(II) compounds with square oxygen coordination (27, 28). The structure of the present Cu(II) complex is not known, but the optical spectra are evidence that the copper atom has essentially square oxygen coordination similar as in the Cu(III) complex.

Trivalent copper is characterized by a d^8 configuration which in D_{4h} symmetry may exist either in a high spin configuration with a $^3B_{1g}$ ground state arising from a ^3F state of the free ion or in a low spin configuration with a $^1A_{1g}$ ground state arising from a ^1G excited state of the free ion. From magnetic measurements it is known that the complex is diamagnetic (29) revealing that the $^1A_{1g}$ state is the ground state of copper in the present complex. One possible interpretation of the spectra of $Na_5[Cu(HIO_6)_2]$ is obtained with the help of a ligand field energy diagram for a d^8 system in a ligand field of D_{4h} symmetry with strong tetragonal distortion (30). The diagram was calculated for tetragonal ligand field parameters $D_t = 1000$ cm^{-1} (0.125 eV) and $D_s = 5000$ cm^{-1} (0.625 eV) including spin–orbit interaction with a spin–orbit interaction constant ζ of 650 cm^{-1} (0.081 eV). The Racah parameters were $B = 905$ cm^{-1} (0.113 eV) and $C = 4B$. If one chooses the octahedral ligand field parameter Δ as 25,000 cm^{-1} (3.13 eV) one obtains rough agreement with the experimental data. The first "$d–d$" transition should be a spin-forbidden ($^1A_{1g} \rightarrow {}^3B_{1g}$) transition at ca. 0.63 eV, which might correspond to the sharp band of low intensity at 0.64 eV. The first spin-allowed "$d–d$" transition ($^1A_{1g} \rightarrow {}^1B_{1g}$) at ca. 2.1 eV compares well with the shoulder at 2.2 eV in the diffuse reflectance spectra. The "$d–d$" transitions at higher energies are masked by the intense band near 3 eV. It is assigned to a ligand to metal charge transfer (LMCT) band which corresponds to a reduction of the trivalent to divalent copper. No such low energetic LMCT band is found for the Cu(II) complex. According to Gaussian analysis of the solution spectra (18) another

band is located at 3.6 eV in reasonable agreement with the position of the $^1A_{1g} \rightarrow {}^1E_g$ transition which is predicted to occur at 3.8 eV from the ligand field energy diagram. The $^1A_{1g} \rightarrow {}^1A_{2g}$ transition which should occur at 2.9 eV coincides exactly with the LMCT band and cannot be separated.

Finally the spectrum of the green complex which is supposed to be a Cu(II)/Cu(III) mixed valence compound is discussed. It is readily seen from Fig. 1 that it is indeed composed of the features of the Cu(II) and the Cu(III) complex. On one hand there is the broad band of the "$d–d$" transitions near 2 eV which is characteristic for divalent copper. On the other hand also significant absorption around 3 eV is present which is the superposition of the "$d–d$" bands and the LMCT band of trivalent copper.

In conclusion, in molecular complexes with copper in oxygen environment divalent and trivalent copper can be well distinguished with the help of optical spectroscopy.

3.2 Y_2BaCuO_5 ("green phase")

Y_2BaCuO_5 is well suited for a comparison with $YBa_2Cu_3O_{7-\delta}$ because the crystal structure of Y_2BaCuO_5 contains the copper atoms in fivefold distorted square pyramidal coordination of oxygen atoms which are not directly connected (19). Similar CuO_5 units exist in $YBa_2Cu_3O_{7-\delta}$; however, they form a two-dimensional network. The diffuse reflectance spectra of Y_2BaCuO_5 diluted with $BaSO_4$ are presented in Fig. 3. In the present case the line positions of the pure powder spectra and the spectra of Y_2BaCuO_5 diluted with $BaSO_4$ were in good agreement. The spectra reveal two main areas of absorption. One of them is centered around 1.8 eV with a shoulder around 1.4 eV, the other broad absorption is centered around 3.4 eV. The gross structure of the spectrum is similar to that of the bisperiodato-cuprate(II) (cf. Figs. 1 and 2). The most remarkable difference is that the intensity of the two absorption
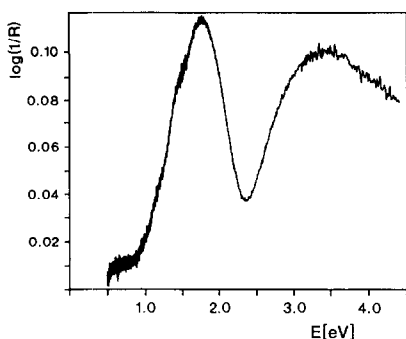
FIG. 3. Diffuse reflectance spectrum of Y_2BaCuO_5 diluted with $BaSO_4$.

ranges in Y_2BaCuO_5 is nearly the same, whereas the lower energy band is of significantly lower intensity in the Cu(II) complex. Shape and energy range support the interpretation of the 1.8-eV band in the spectra of Y_2BaCuO_5 as a superposition of the different "d–d" transitions as in the bisperiodato-cuprate(II). Since the copper atom in Y_2BaCuO_5 exists in a square pyramidal coordination with equatorial Cu–O distances of ca. 2.0 Å and an apical Cu–O distance of 2.2 Å (19) one expects that the $x^2 - y^2$ and the z^2 orbitals are highest in energy. Consequently the $z^2 \to x^2 - y^2$ transition will be lowest in energy and may give rise to the 1.4-eV shoulder of the 1.8-eV band. Further it is expected that the xz and yz orbitals are slightly lower in energy than the xy orbital. The different transitions from these orbitals into the $x^2 - y^2$ orbital, however, are not resolved and their superposition gives rise to the 1.8-eV feature. The absorption above 3 eV is probably of $O(p)$–$Cu(d)$ LMCT character.

Though absolute intensities cannot be estimated from the present diffuse reflectance spectra, the nearly equal intensity of high and low energy absorptions is evidence for a high intensity of the "d–d" transitions in Y_2BaCuO_5. The distorted square pyramids in Y_2BaCuO_5 are asymmetric. Therefore the

"d–d" transitions are neither parity- nor symmetry-forbidden.

3.3 $YBa_2Cu_3O_6$

As has been pointed out in the introduction $YBa_2Cu_3O_6$ contains copper in two different coordinations which should give rise to different optical response. In Fig. 4 the transmittance spectra of a thin film of $YBa_2Cu_3O_6$ on MgO at room temperature and at liquid helium temperature are shown. The overall spectra are in good agreement with those obtained previously for thin films on sapphire (17), for ceramic samples, and for single crystals (12–15). The room temperature spectra reveal three bands around 1.7, 2.6, and 4 eV, respectively. In the low temperature spectra additional features around 2.1, 3.8, and 4.4 eV are resolved. The origin of the 1.7- and 2.6-eV structures has been a matter of controversy. Geserich et al. (17) suggested that they are due to "d–d" transitions of divalent copper, whereas Garriga et al. (13) in view of their rather great intensity attributed them to low lying charge transfer transitions in the copper–oxygen planes. The present well-resolved low temperature spectra reveal an additional peak
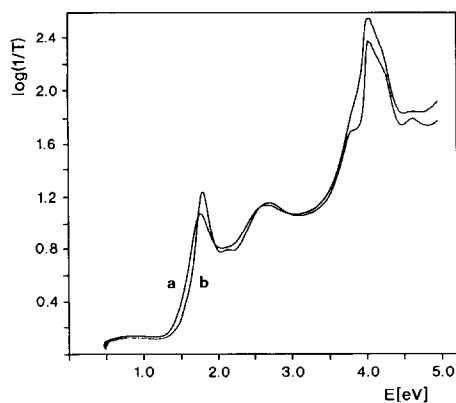

FIG. 4. Transmittance spectra of a thin film of $YBa_2Cu_3O_6$ deposited on a MgO substrate (a) at room temperature and (b) at liquid helium temperature.

at 2.1 eV. Similar to Y_2BaCuO_5, the sharp peaks at 1.7 and 2.1 eV are in the energy range of the "d–d" transitions typical for divalent copper. Divalent copper in $YBa_2Cu_3O_6$ is only expected at the Cu(2) sites where the Cu atom has C_{4v} site symmetry. The only "d–d" transition which is electronically allowed in C_{4v} symmetry is the $^2B_1 \rightarrow {}^2E$ transition. Therefore the intense peak at 1.7 eV, the intensity of which increases with decreasing temperature, is assigned to the $^2B_1 \rightarrow {}^2E$ transition. Since the equatorial Cu–O distance is much shorter than the apical one the xy orbital is certainly higher in energy than the xz and yz orbitals are. Thus the weaker 2.1-eV peak most probably corresponds to the $^2B_1 \rightarrow {}^2A_1$ transition. The $^2B_1 \rightarrow {}^2B_2$ transition should be lowest in energy and might become visible in the low temperature spectra as a small shoulder around 1.55 eV in the low energy tail of the 1.7-eV band. These arguments lead to the d orbital sequence $x^2 - y^2 > xy > xz, yz > z^2$ for the Cu(2) sites in $YBa_2Cu_3O_6$. The above assignments are also in accord with the differences between the coordination polyhedra of $YBa_2Cu_3O_6$ and Y_2BaCuO_5. In the latter the $z^2 \rightarrow x^2 - y^2$ transition was suggested to be lowest in energy and attributed to the 1.4-eV shoulder in Y_2BaCuO_5. In $YBa_2Cu_3O_6$ the mean equatorial Cu–O distance is about 0.06 Å shorter than in $Y_2Ba CuO_5$ while the apical Cu–O distance is about 0.25 Å larger. Consequently the interaction of the d electrons with the ligands is increased in the xy plane while the interaction along the z-axis due to the apical oxygen atom is much smaller. These effects will result in a certain destabilization of the $x^2 - y^2$ and xy orbitals, a certain stabilization of the xz and yz orbitals, and a significant stabilization of the z^2 orbital in the CuO_5 units of $YBa_2Cu_3O_6$ in comparison with Y_2BaCuO_5. The overall splitting of the d orbitals should be increased in $YBa_2Cu_3O_6$. These effects will be even more pronounced in cuprates with square copper–oxygen coordination in

agreement with the electronic spectra of Li_2CuO_2 which contains square planar CuO_4 entities (31). Peaks at 1.8, 2.1, and 2.6 eV were observed and assigned to the $^2B_1 \rightarrow {}^2B_2$, $^2B_1 \rightarrow {}^2E$, and $^2B_1 \rightarrow {}^2A_1$ transitions, respectively. The broad intense peak at 2.6 eV in the spectra of $YBa_2Cu_3O_6$, however, is most probably the lowest energy LMCT band corresponding to the 3.4-eV feature in Y_2BaCuO_5.

The most prominent peak in the spectra of $YBa_2Cu_3O_6$ occurs around 4 eV. Based on comparison with the spectra of $YCuO_2$ which also contains linear O–Cu–O units Kelly et al. (32) suggested that this transition involves the O(1)–Cu(1)–O(1) dumbbells. Recently Kircher et al. (15) investigated the anisotropy of the dielectric function by ellipsometric measurements on an $YBa_2Cu_3O_6$ single crystal. From comparison with band structure calculations the 4-eV peak was assigned to a transition involving the Cu(1) atom which has mainly $3d^{10} \rightarrow 3d^9 4p$ character. These assignments are in agreement with the fact that the intensity of the 4-eV peak decreases with increasing oxygen content (12, 13) which corresponds to the oxidation of the monovalent copper at the Cu(1) site. The 3.8-eV peak was observed in the ellipsometric spectra too (15). It was also assigned to a mainly intraionic transition of monovalent copper.

3.4 $YBa_2Cu_3O_7$

Figure 5 reveals that the electronic spectra of the conducting and (below 90 K) superconducting $\delta = 0$ phase are completely different from those of the semiconducting $\delta = 1$ phase. The spectra are dominated by a continuous absorption extending over the whole spectra range. The sharp peaks which were attributed to the "d–d" transitions of divalent copper atoms within the $Cu(2)O_2$ planes have vanished. Instead broad regions of absorption in the near IR, around 1.4 and 3 eV, and in the near UV occur. The spectra
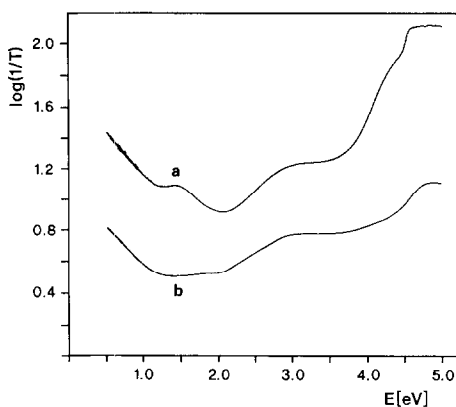
FIG. 5. (a) Transmittance spectrum of a thin film of $YBa_2Cu_3O_{7-\delta}$ ($\delta < 0.1$) on a MgO substrate at liquid helium temperature. (b) Transmittance spectrum of a thin film of $YBa_2Cu_3O_{7-\delta}$ with a broad superconducting transition ($\Delta T_c \approx 20$ K) at room temperature.

below and above T_c do not reveal significant differences.

First, the question arises whether there is evidence for Cu(III) in the spectra of $YBa_2Cu_3O_7$ which can be expected from stoichiometry. It has been elaborated in Section 3.1 that trivalent copper in oxygen coordination exists in a d^8 low spin configuration which does not give rise to low energetic "d–d" transitions (with the exception of spin-forbidden "d–d" transitions of low intensity). The first intense absorption in the bisperiodato-cuprate(III) was a broad band near 3 eV which is a superposition of the first "d–d" transitions and a LMCT transition. In the spectra of $YBa_2Cu_3O_7$ a broad band near 3 eV occurs, the shape and energetic position of which differs significantly from the 2.6-eV peak in $YBa_2Cu_3O_6$ (cf. Figs. 4 and 5). This feature may be a hint for Cu(III). This assignment, however, only makes sense if discrete valences can still be attributed to the atoms, which is only possible for mixed-valence compounds with rather small interatomic coupling [Class II mixed-valence compounds according to the classification of Robin and Day (33)]. On

the other hand the transitions which were attributed to "d–d" transitions of divalent copper in the $Cu(2)O_2$ planes have vanished. From the chemical point of view it seems reasonable to consider the $Cu(2)O_2$ planes as an extended intermediate valence system (Class III according to Robin and Day), the electronic spectra of which do not reveal the electronic transitions associated with the individual valences. If the 3-eV feature really corresponds to static or fluctuating Cu(III) it should be rather attributed to the Cu(1) sites. This is also compatible with the short Cu(1)–O(1) distance which is more characteristic for monovalent and trivalent copper than for divalent copper.

The broad absorption in the near IR is characteristic for all the different classes of mixed-valent oxocuprates, for samples revealing superconductivity as well as for those which do not (16, 34, 35). It is usually attributed to the free carrier absorption. An interpretation as an intervalence band has also been suggested (36). A further remarkable feature is the peak at 1.4 eV in the spectra of $YBa_2Cu_3O_7$ which is not simply the 1.7-eV "d–d" transition shifted to lower energies as has been proposed (16, 17). This becomes clear from the spectra of a thin film of $YBa_2Cu_3O_{7-\delta}$ with a broad superconducting transition (transition width of ca. 20 K, T_c^{on} of 85 K) which is presumably a consequence of a greater δ-value (Fig. 5). The 1.7-eV peak is still seen as a small feature above the continuous background. Its position is essentially unchanged in comparison with $YBa_2Cu_3O_6$. The 1.4-eV peak has no considerable intensity. This result is in agreement with ellipsometric spectra of $YBa_2Cu_3O_{7-\delta}$ with variable δ which also reveal the decrease of intensity of the 1.7-eV feature with decreasing δ (12). Therefore the 1.4-eV peak seems to be a different feature characteristic of samples with high oxygen content. A similar absorption, the intensity of which increases with increasing x, is found in the

spectra of $La_{2-x}Sr_xCuO_4$ (35) which does not contain the Cu(1)-type atoms. Thus it is likely that the 1.4-eV feature corresponds to an electronic transition within the delocalized electron system in the copper–oxygen planes.

4. Conclusions

In this study we first investigated the electronic spectra of complexes with periodate ligands in order to establish the spectral characteristics of divalent and trivalent copper in oxygen atom environment. The spectra of $Na_5[Cu(HIO_6)_2]$ as well as its diamagnetism are compatible with the assumption of a d^8 low-spin configuration of the central ion. The spectra of the Cu(II) complex reveals a broad band around 2 eV which is the superposition of the "d–d" transitions associated with the d^9 configuration of the central ion. In the spectra of the insulating or semiconducting oxocuprates Y_2BaCuO_5 and $YBa_2Cu_3O_6$ characteristic absorptions in this energy range also occur. Considering the splitting of the transitions it is likely that they are due to the "d–d" transitions of divalent copper too. Based on intensity arguments the energy sequence of the d orbitals at the Cu(2) sites in $YBa_2Cu_3O_6$ was derived. From our results it seems that the electronic situation in these compounds is similar as in insulating NiO where "d–d" transitions as in Ni-complexes in solution are found (37). In NiO the d electrons are believed to be localized and to form an atomic-like narrow band in contrast to what is expected from one-electron band theory (5).

The features which were attributed to individual Cu(II) are lost in the spectra of metallic $YBa_2Cu_3O_7$. Instead new features occur. It is reasonable to consider the copper–oxygen planes as an intermediate valence system with its own spectral characteristics. Comparison with the spectra of the bisperiodato-cuprate(III) shows that Cu(III) at the Cu(1) sites may give rise to a feature around 3 eV. Since it is, however, difficult to distinguish between resonances due to Cu(1) and due to Cu(2) sites the role of the Cu(1) sites for the electronic properties of $YBa_2Cu_3O_7$ cannot be elucidated clearly from the present work.

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