THE COLOR OF POLARIZATION IN CUPRATE SUPERCONDUCTORS

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A technique for the identification of individual anisotropic grains in a heterogeneous and opaque material involves the observation of grain color in reflected light through crossed polarizers (color of polarization). Such colors are generally characteristic of particular phases. When grains of many members of the class of hole-carrier cuprate superconductors are so viewed at room temperature with a 'daylight' source, a characteristic color of polarization is observed. We have studied this color in many of these cuprate superconductors and found a strong correlation between color and the existence of superconductivity. We have also examined two members of the electron cuprate superconductors and found that they possess the same color of polarization as the hole-carrier cuprate superconductors so far examined. The commonality of the characteristic color regardless of charge carrier indicates that the presence of this color is independent of carrier type. The correlation of this color with the existence of superconductivity in the cuprate superconductors suggests that the origin of the color relates to the origin of superconductivity.

Using photometric techniques, we have quantified the color of polarization in the superconductors $ErBa_2Cu_3O_7$ and $Bi_2Sr_2CaCu_2O_8$. Reflectivity measurements have been made with a tungsten-halogen light source (3400 K color temperature) on a series of $ErBa_2Cu_3O_{7-x}$ samples, where $0.1 \leq x \leq 0.7$, so as to include both tetragonal insulators and orthorhombic superconductors. Using a simple model, the data have been iteratively fitted with smooth curves to represent the spectra for visible wavelengths. From these curves, we have calculated the coordinates on a chromaticity diagram. The colors compare well with those observed visually. The fits are consistent with ellipsometry and transmissivity results and are compared with the absorption characteristics of Cu^{2+} and Cu^{3+}. We have shown that the structure observed by ellipsometry at ~2.1 eV is apparently a combination of an absorption band in the CuO_2 planes and an extension of the free-carrier distribution into the visible. A second absorption band, also in these planes, appears to shift to higher energy with increasing oxygen concentration in $ErBa_2Cu_3O_{6-7}$ and is present in $Bi_2Sr_2CaCu_2O_8$. This band subtracts blue from the white light reflected, thereby contributing the yellow component of the characteristic golden color of the cuprate superconductors. Both absorption bands are apparently of 3d x^2-y^2 type.

1. INTRODUCTION

The processing of single crystals, polycrystalline bulk, or thin films to produce electronic devices quickly and efficiently out of the copper oxide, high-transition temperature (T_c) superconductors can be assisted by microscopic examination. The differentiation at room temperature of the $YBa_2Cu_3O_7$-type superconducting phase on a crystal-by-crystal basis can benefit from the optical observation of twinning in the orthorhombic superconductors (1). But the presence of untwinned grains or areas of grains and the production of untwinned (1) or detwinned material (2) makes phase identification more difficult. Optical examination of both hole-carrier (3) and electron (4,5) cuprate superconductors has led to the discovery that, generally, these materials have the same characteristic color when viewed through crossed polarizers (polarization color).

Many opaque, anisotropic materials, with unique structures and compositions, have their own characteristic polarization color (6). However, if the structure or composition is changed, the polarization color generally changes or disappears. For the various cuprate superconductors, from, e.g., $Nd_{1.85}Ce_{0.15}CuO_{4-x}$ (T_c ~ 23 K) to $Tl_2Ba_2Ca_2Cu_3O_{10}$ (T_c ~ 125 K), regardless of changes in structure or

composition, as long as the material contains CuO_2 planes and is superconducting, the same brownish yellow (golden) polarization color is observed.

If the concentration of free-carriers (produced by doping the precursors) is reduced to produce an insulator either by changing the copper, oxygen or cation dopant concentration, the golden color also disappears (3). The change in color from golden to colorless (precursor) occurs for $YBa_2Cu_3O_7$-type materials (3) and for other cuprate superconductors (3,7).

With the sequence of polarization colors well studied and applicable to hole-carrier cuprate superconductors, and perhaps to negative carrier type, it is important to determine the likely band shifts taking place throughout the visible energy range in the Cu^{2+} 3d x^2-y^2 orbitals that combine with the oxygen 2p to construct the CuO_2 planes. We present here a more in depth examination of reflectivity data taken on representative individual grains of $ErBa_2Cu_3O_7$ and $Bi_2Sr_2CaCu_2O_8$ and propose a simple model in an effort to understand the color changes that correlate with superconductivity.

2. MODEL

In order to consider correlating the characteristic golden polarization color to absorption bands or reflection due to free carriers, it is necessary to show directly or by process of elimination that only such phenomena can account for the color. Table 1 contains a list of phenomena including structural ones that have been eliminated as possible origins for the golden color or its coupling with superconductivity. (The structural effect, or lack, of buckling of the CuO_2 planes has not been considered.) Generally, from Table 1 by process of elimination, only a combination of phenomena in a relatively specific arrangement is likely to result in both superconductivity and the golden color. Structurally then, the color originates from the two-dimensional CuO_2 planes by absorption and/or reflectance only. Apparently, the varying indices of refraction play no part in the production of color.

Because the superconductor to insulator sequence of polarization colors is, so far, reproducible for doping by alkaline earth cation, oxygen, or replacement of Cu, determining the various copper-oxygen colors and possible copper-oxygen absorption bands that may produce these colors can be aided by noting the colors of similar Cu oxide materials. Table 2 contains a list of impurity phases observed in various cuprate systems which contain superconductors.

The colors observed for various copper oxide containing phases (Table 2) suggests that absorption bands may exist in the visible. Note that the color of polarization of Bi_2CuO_4 is red. Absorption bands in the blue and green (or a large band across both) could produce this color. CuO is blue which may be due to absorption bands in the red-green. The R_2BaCuO_5 (2-1-1) phase has a green color which may be due to the presence of both an absorption band in the red and one in the blue. For those phases with Cu^{2+} present, absorption bands in the blue, green and red in various combinations would account for the colors and indicate that Cu^{2+} can disperse throughout the visible. A variety of colors, changing probably with orientation, for a given phase may have an origin in both birefringence and differential absorption.

As the origin of the characteristic color is a two dimensional structure within the various cuprate superconductors, spectroscopic data on various two-dimensional Cu^{2+} and perhaps Cu^{3+} complexes in aqueous solution are expected to indicate likely absorption bands contributing to the color and the color changes from precursor to superconductor. Table 3 contains absorption band parameters for Cu^{2+} and Cu^{3+} in the visible (700-400 nm, 1.77-3.10 eV, 14300-25000 cm^{-1}) to near visible range. To produce a yellow color by absorption, there need only be an absorption band in the blue range (white minus blue produces yellow). The golden color is in part due to yellow (4). The absorption bands included in Table 3 from Cu^{3+} are in the violet, which suggests that the presence of the yellow component may be due to charge transfer. For absorption bands to account for the color in Bi_2CuO_4 (red), either a large band extending across the blue-green range or two bands, one in the blue and one in the green, are needed. The necessity of a blue absorption band contributing to produce the green color of the 2-1-1 phase has also

Table 1 Origin of the Copper Oxide Superconductor Color of Polarization

Possibility	Comment
Water contamination (surface contamination)	color seen in unpolished thin films of $RBa_2Cu_3O_7$, freshly broken single crystals, and in $Bi_2Sr_2CaCu_2O_8$ which is not readily affected by water. Auger electron spectroscopy of such surfaces has shown only slight carbon contamination. Freshly fractured and ion milled surfaces show the color.
Instrument characteristics	color seen in reflection with other types of polarizing microscopes, as long as a 'daylight' source is used and polarizers are crossed.
Grain size effect	color seen in thin films (~1μm) to crystals 3 mm x 1 mm.
Depth of penetration	reflectivity measurements on progressively thicker films of $RBa_2Cu_3O_7$ have shown the light penetration depth to be on the order of several hundred nanometers. Even if the first few atomic layers are not superconducting, much of the reflected light seen is coming from greater depth.
Three dimensional structure	color not seen in ordinary illumination (bright field) nor in total reflectance measurements.
Presence of copper oxide alone	CuO (tenorite) has a blue color of polarization.
Perovskite structure	color not seen in $BaTiO_3$ or in $RBa_2Cu_3O_6$.
Copper oxide chains	color seen in $Bi_2Sr_2CaCu_2O_8$ and $Tl_2Ba_2Ca_2Cu_3O_{10}$ which have no long range chains.
CuO_2 planes	color not seen in $RBa_2Cu_3O_6$, which has CuO_2 planes.
Orthorhombic structure	color seen in tetragonal $Tl_2Ba_2Ca_2Cu_3O_{10}$ and not in La_2CuO_4 which is orthorhombic and blue(purple).
Presence of rare earth	$Bi_2Sr_2CaCu_2O_8$ and $Tl_2Ba_2Ca_2Cu_3O_{10}$ do not contain them.
Presence of an alkaline earth	$RBa_2Cu_3O_6$ contains an alkali earth and is not a superconductor. $Nd_{1.85}Ce_{0.15}CuO_4$ does not contain an alkaline earth.
Apical oxygen	absent in $Nd_{1.85}Ce_{0.15}CuO_4$.
Electron holes	$Nd_{1.85}Ce_{0.15}CuO_4$ is an electron superconductor.
Cu^{1+} state	Cu_2O, when a distorted cubic due to impurities, is red.
Cu^{2+} state	Bi_2CuO_4 is red, Er_2BaCuO_5 is green and CuO is blue.
Cu^{3+} state	unlikely in $Nd_{1.85}Ce_{0.15}CuO_4$ or $Pr_{1.85}Ce_{0.15}CuO_4$.

Table 2 Colors Through Crossed Polarizers of Impurity Phases in Superconductor Materials

Material	Color
Cu_2O	red
CuO	blue
Bi_2O_3	orange-yellow
Pb_3O_4	orange
Ba cuprate	remains dark as stage is rotated
Bi_2CuO_4	red
R_2BaCuO_5	green
Sr_2CuO_3	white-purple-aqua blue
$(Sr,Ca)_2CuO_3$	white-purple-aqua blue
Ca_2CuO_3	pale yellow-white
$(Ca,Sr)_2CuO_3$	pale yellow-white
Bi-Sr-Ca-O	colorless

been suggested. The presence of an absorption band in the blue range may occur for Cu^{2+}.

Table 3 Near Visible Absorption Band Parameters for Cu^{2+} and Cu^{3+} in Complexes (8,9)

Complex	Geometry	Extinction Coefficient $M^{-1}cm^{-1}$	Peak Centroid cm^{-1}	Half Width Half Maximum cm^{-1}	
$(NO_3)_2$	square planar	12.85	12630	1979	
$(NO_3)(NH_3)$	square planar	93.00	15670	2271	
$(NH_3)_4$	square planar	54.00	16900	2542	
$(HIO_6)_2$	square planar	90.28	23750	2878	(Cu^{3+})
$(H_2TeO_6)_2$	square planar	73.68	24880	4101	(Cu^{3+})

For any phase that is semiconducting or metallic, an increase in overall reflectivity may occur due to the presence of free carriers. But the presence of free carriers alone is not responsible for the golden color or

superconductivity. The metallic $La_5SrCu_6O_{15}$ material is anisotropic, white (3) and not superconducting. A relatively uniform distribution of free carriers throughout the visible can reflect white.

We have found by optical inspection of tetragonal $ErBa_2Cu_3O_6$ (colorless) single crystals (~0.5 mm x ~0.5 mm) and very thin, on the order of ~1 μm, that in ordinary reflected light the crystals are opaque. When viewed through crossed polarizers at maximum brightness, they are sufficiently transparent to allow the surface beneath to be seen. Apparently, as the $ErBa_2Cu_3O_6$ phase is undoped, either the production of absorption bands or the presence of free carriers limits the depth of penetration of polarized light. From previous reflectivity (10) and ellipsometry (11), the free carrier distribution is limited primarily to the infrared, with some extension into the visible. For reflectivity measurements on $YBa_2Cu_3O_7$-type superconductors and other cuprate superconductors, a continuously increasing reflectivity from approximately the yellow (~2.1 eV, ~580 nm) into the infrared is expected.

The spectroscopic measurements made on various copper complexes are obtained in transmission. Since the optical density measurements (transmissivity) on $YBa_2Cu_3O_7$-type superconductors (10) have the same structural features as obtained in reflectivity measurements (4,10), it is reasonable to assume that at least across the visible range structures in reflected spectra (through crossed polarizers) are the same, except for intensity, as those in transmitted spectra (through crossed polarizers). The reflectivity (R), then, can be described in the same way as optical density with $R = I/I_o$:

$$R = 10^{-c\varepsilon}, \tag{1}$$

where c is the molar concentration of the two-dimensional (or less) color producing structure and ε is the extinction coefficient. The reflectance (I) through crossed polarizers for each grain measured is normalized to the white reflectance (I_o) spectrum of a powdered Si oxide standard (4).

In general any absorption band can be approximated with a gaussian function. The gaussian expression we have chosen to use is as follows:

$$\varepsilon = \varepsilon_{Max} e^{-(\nu-\nu_{Max})^2/\theta^2}, \tag{2}$$

where ε_{Max} is the extinction coefficient, ν_{Max} is the centroid position and θ is the half width at half maximum in wavenumbers for a particular absorption band. In all the colors exhibited by the various cuprates (Table 2), a minimum of two absorption bands are needed, generally. In addition, the presence of free-carriers is expected to increase reflectivity. If each of these components occurs, the complete expression for the extinction coefficient is as follows:

$$\varepsilon = \varepsilon_{Max1} e^{-(\nu-\nu_{Max1})^2/\theta_1^2} + \varepsilon_{Max2} e^{-(\nu-\nu_{Max2})^2/\theta_2^2} - \varepsilon_{Max3} e^{-(\nu-\nu_{Max3})^2/\theta_3^2}. \tag{3}$$

Since the individual ε_{Maxi} are not known, a combined factor of $\varepsilon_{Maxi}c$ is obtained and referred to as an extinction/reflection coefficient. Iterative fitting is accomplished by applying first a single gaussian function, then two and finally three, if required, to conform to the structures apparent in the data.

3. EXPERIMENTAL

The preparation of $ErBa_2Cu_3O_{6+x}$ and $ErBa_2Cu_3O_{7-x}$, examined by reflectivity (4), the $Bi_2Sr_2CaCu_2O_8$ (BiSCCO, T_c ~ 85 K, R_0 ~ 75 K), $Tl_2Ba_2Ca_2Cu_3O_{10}$ (T_c ~ 120 K) and $Nd_{1.85}Ce_{0.15}CuO_{4-x}$ (T_c ~ 23 K) samples has been described (3,4). The same microscope-monochromator arrangement for the reflectivity measurements (4) has been used to measure reflectivity on BiSCCO, $Tl_2Ba_2Ca_2Cu_3O_{10}$ (T_c ~ 120 K) and $Nd_{1.85}Ce_{0.15}CuO_{4-x}$ (T_c ~ 23 K). Preliminary reflectivity data have been taken on a few representative

grains per sample. Representative spectra are plotted and iteratively fitted with smooth curves. The reflectivity data are considered as preliminary because the light levels involved are close to the lower detection limit which may increase error.

4. RESULTS

Representative reflectivity spectra for BiSCCO and for $ErBa_2Cu_3O_{6-7}$ versus oxygen concentration are shown in Figure 1.

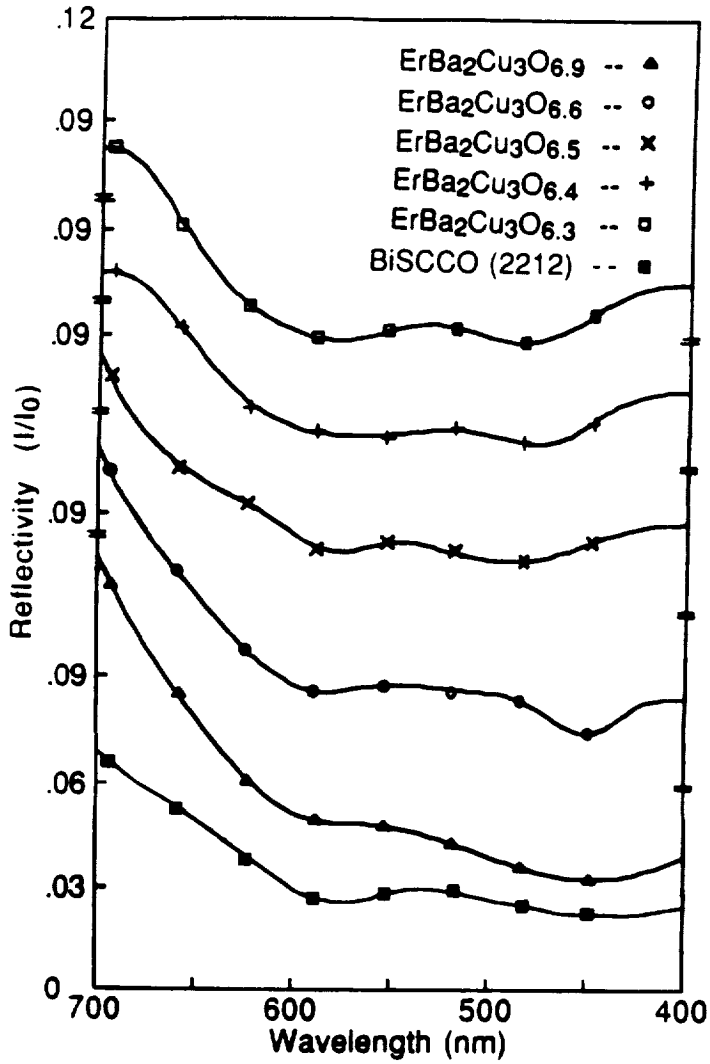

Figure 1 Reflectivity spectra for $ErBa_2Cu_3O_{6.3}$, $ErBa_2Cu_3O_{6.4}$, $ErBa_2Cu_3O_{6.5}$, $ErBa_2Cu_3O_{6.6}$, $ErBa_2Cu_3O_{6.65}$ and $ErBa_2Cu_3O_{6.9}$ (identical spectra, only one plotted), and $Bi_2Sr_2CaCu_2O_8$. The smooth curves plotted through the data have been iteratively fitted.

The preliminary reflectivity data from $Tl_2Ba_2Ca_2Cu_3O_{10}$ and $Nd_{1.85}Ce_{0.15}CuO_{4-x}$ show structures similar to those in Figure 1, but some portion of the spectra may be due to impurities because the aperture size is much larger than that of the individual grains in these samples.

Each data set has been fit successively and alternately with one, two or three gaussian functions to confirm that only the use of three gaussians can conform to the structures apparent in the spectra. The resulting parameters are listed in Table 4. The chromaticity coordinates have been calculated for each spectrum using the smooth curves of the iterative fits. These have been plotted on a chromaticity diagram in which

the color (hue) fields are delineated. In general, the resulting colors agree well with those observed visually and recorded on film (3). Only the data obtained on the $ErBa_2Cu_3O_{6.5}$ grains is on the border between the orange-red (brown) field and the yellow-orange (golden) field suggesting the presence of both orthorhombic and tetragonal material within the grains.

Table 4 Fitting Parameters for Reflectivity on Cuprate Phases

Phase	Absorb (-) Reflect (+)	Extinction/ Reflection Coefficient	Peak Centroid cm^{-1}	Half Width Half Maximum cm^{-1}	T_c
$ErBa_2Cu_3O_{6.3}$	+	0.27	14400	1100	---
(Blue/Purple)	-	0.19	17200	1400	
(940°C)	-	0.205	20650	1900	
$ErBa_2Cu_3O_{6.4}$	+	0.35	14500	1500	---
(Brown)	-	0.165	16800	3600	
(800°C)	-	0.14	21200	1500	
$ErBa_2Cu_3O_{6.5}$	+	240	0	5600	~50 K
(Golden)	-	0.12	17200	800	
(710°C)	-	0.16	20400	2200	
$ErBa_2Cu_3O_{6.6}$	+	15.7	0	7600	~63 K
(Golden)	-	0.095	16800	1000	
(610°C)	-	0.14	22200	1100	
$ErBa_2Cu_3O_{6.65}$	+	12.8	0	7800	~85 K
(Golden)	-	0.072	16700	1100	
(500°C)	-	0.15	22300	3000	
$ErBa_2Cu_3O_{6.9}$	+	12.8	0	7800	~95 K
(Golden)	-	0.072	16700	1100	
(25°C)	-	0.15	22300	3000	
$Bi_2Sr_2CaCu_2O_8$	+	5.7	0	8600	~85 K
(Golden)	-	0.15	17100	1100	
	-	0.10	22300	3000	

5. DISCUSSION

The estimated percent error based on reproducibility for reflectivity is approximately 5 % overall, with a lower value for reflectivity above 9 %. The increased error below $R \approx 0.09$ is assumed to be due to light levels at or just above the lower limit for the detector. Generally, for so few points (eight) per spectrum only a single gaussian (three variables) would be warranted. However, for the most part, there has been structural reproducibility between grains of the same sample and between samples which suggests that the fluctuations across the spectra are not random. A two-gaussian function (one for absorption at high energies and one for reflection at low energies) cannot account for the structure at ~590 nm (~2.1 eV) between them. At the high-energy end (violet range) for the superconductors $ErBa_2Cu_3O_{6.9}$ and $Bi_2Sr_2CaCu_2O_8$, the absorption band may extend further into the ultraviolet. See Figure 1.

Figure 2 is a plot of the centroid shifts relative to the centroid of the two end-point superconductors $ErBa_2Cu_3O_{6.9}$ and $Bi_2Sr_2CaCu_2O_8$ for the absorption band at the high-energy end of the visible range. Although there appears to be a systematic shift in this band with increasing oxygen content which

compares with a similar shift observed by ellipsometry (12), the measurement on $ErBa_2Cu_3O_{6.5}$ is an exception. If the shift is confirmed by forthcoming measurements using a more sensitive photomultiplier (detector) and a xenon 'daylight' source on homogeneous materials, then the likely position of the band for $ErBa_2Cu_3O_{6.0}$ is at ~19000 cm^{-1} (~520 nm, ~2.4 eV). This amounts to a shift of 0.4 eV from ~2.4 eV to ~2.8 eV, whereas ellipsometric results found a shift from ~2.6 eV to ~2.8 eV (12), with increasing oxygen. This band also appears to widen with increasing oxygen, see Table 4. The shift of the band to higher energy, near those of Cu^{3+} (see Table 3) suggests a charge-transfer band, although the apparent location in the blue range, instead of violet, may indicate a Cu^{2+} band that is only partially of a charge-transfer nature. The presence of this 3d x^2-y^2 band in the reflectivity and its necessity for the production of the golden color of the electron superconductors tends to preclude it being solely a Cu^{2+} to Cu^{3+} charge-transfer band. The band is independent of the type of charge transferred and apparently energy symmetric ($Cu^{1+} \leftrightarrow Cu^{2+} \leftrightarrow Cu^{3+}$).

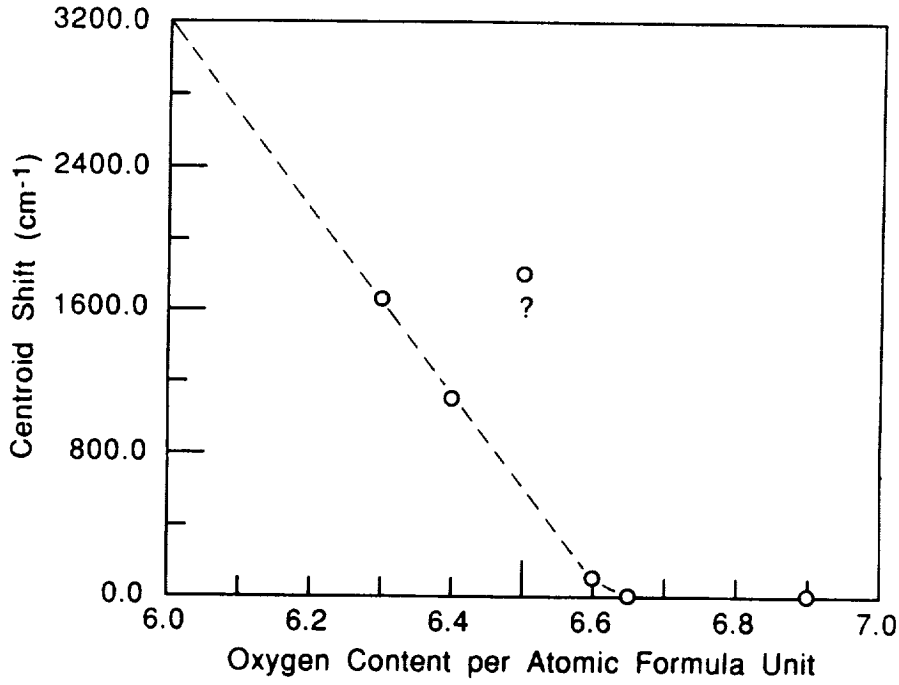

Figure 2 Plot of the centroid shifts for the absorption band at the high-energy end obtained from the iterative fits to the reflectivity data on the $ErBa_2Cu_3O_{6-7}$ samples. The position of the centroid for the two end-point superconductors $ErBa_2Cu_3O_{6.9}$ and $Bi_2Sr_2CaCu_2O_8$ is taken as zero.

Previous reflectivity (10) and ellipsometry (11,12) have reported a structure at ~2.1 eV that appears to vary with oxygen concentration in $ErBa_2Cu_3O_{7-x}$ and may be affected by out-of-plane oxygen (11). It also occurs in BiSCCO, see Figure 1. From the parameters listed in Table 4, there is an absorption band centered at ~2.1 eV (17000±200 cm^{-1}, with half width at half maximum of 2500±900 cm^{-1}), which does not shift with changes in the oxygen concentration, but decreases in apparent intensity (decrease in extinction/reflection coefficient) as the free carrier concentration increases. The location and width of this band corresponds with a band observed for the molecular complex $Cu(NH_3)_4$, $(H_2O)_2^{2+}$ (8), see Table 3, in the plane between Cu^{2+} and NH_3^{1-}. As it is a Cu^{2+} 3d x^2-y^2 band in $Cu(NH_3)_4$, $(H_2O)_2^{2+}$, it is presumed to be so in the cuprate CuO_2 planes between Cu^{2+} and oxygen. Variations in the structure may be due in part to the extension of the free-carrier distribution into the visible and to the systematic intensity decrease (decreased extinction/reflection coefficient, see Table 4) of the band with increasing oxygen content.

With regards to the three structures observed across the visible, we note that ellipsometry measurements (in the superconducting and normal state) at 7 K and 300 K (12) show no significant shifts in any of the three structures indicating that the golden color remains below T_c.

6. CONCLUSIONS

Using a simple model based on gaussian functions to represent absorption bands and reflectivity by free carriers preferentially distributed primarily in the infrared, we have iteratively fitted reflectivity data for $ErBa_2Cu_3O_{6.9}$ and $Bi_2Sr_2CaCu_2O_8$ superconductors. By comparing these fits to those obtained from $ErBa_2Cu_3O_{6-7}$ and to known bands for Cu^{2+} and Cu^{3+}, we have shown that the structure observed with ellipsometry at ~2.1 eV is apparently due to an absorption band in the CuO_2 planes, which decreases in intensity with increasing oxygen concentration, and the extension of the free-carrier distribution into the visible. A second absorption band, also in these planes, appears to shift to higher energy with increasing oxygen concentration in $ErBa_2Cu_3O_{6-7}$ and is present in $Bi_2Sr_2CaCu_2O_8$. This band subtracts blue from the white light reflected, thereby contributing the yellow component of the golden color characteristic of both electron and hole-carrier cuprate superconductors. Both bands are apparently of 3d x^2-y^2 type. The colors calculated from the iterative fits to the reflectivity data generally correspond with the colors observed visually and recorded on film using a 'daylight' source.

7. ACKNOWLEDGMENTS

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