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Optical gap of CuO

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The optical absorption edge of CuO single crystals has been investigated by reflectance and transmittance measurements at different temperatures. An exponential decay of the absorption has been detected, while temperature dependence of the edge and of the steepness between 10 K and room temperature indicate a large coupling of electronic states with lattice vibrations. At the lowest temperatures, excitonic structures have been revealed.

I. INTRODUCTION

Cupric oxide is a semiconducting compound that has been studied early, together with the other copper oxides, for photothermal or photoconductive applications.[1–3] In recent years it has attracted much interest, because of being the basis of several high-T_c superconductors.[4–6]

In effect, some characteristics like the crystalline structure (in particular, the copper-oxygen coordination), as well as the thermodynamic and magnetic properties, are very similar in CuO and high T_c superconductors. Moreover, copper oxide itself exhibits very peculiar features: magnetic fluctuations, magnon-photon interactions, phase transitions, and instabilities with respect to the stoichiometry.[7,8]

On the other hand, not much is known up to now about the electronic structure of this material. As regards optical investigations, recent data mainly concern far infrared properties and Raman scattering both on single crystals and pellet samples.[9–11] The interband part of the optical spectrum, and, in particular, the absorption edge, has been studied only at room temperature on polycrystalline samples or on thin films obtained by sputtering or thermal oxidation. The results strongly depend on the sample preparation and on the measurement technique used; the reported values of the gap energy range between 1.21 and 1.5 eV and in some cases a shallow absorption edge is mentioned.[12–18] Recently, in a study of the optical absorption in the medium infrared, it was indicated that a relatively large change of the gap occurs with the temperature.[8]

In the present work, we present a set of measurements at the optical absorption edge performed at several temperatures between 10 and 300 K on single crystalline samples of CuO. The energy dependence of the absorption in the vicinity of the absorption edge has been investigated.

II. EXPERIMENT

Single crystalline samples were prepared with the flux method described elsewhere.[19] The samples were analyzed with x-ray diffraction revealing no spurious phases and monoclinic crystallographic order with lattice parameters (a=4.6859 Å, b=3.4283 Å, c=5.1232 Å, and β=99.541°), in very good agreement with the ones reported in the literature.[20]

A single crystal with a polished facet lying along the b-c plane was used to measure the bulk reflectivity with light polarized along the c and b axis, respectively. Such results were controlled on several other crystals with surfaces oriented along different crystallographic directions. Ellipsometric measurements, performed on the same samples in the energy range 1.4–5 eV, also confirm the measured reflectivity.

Among the samples extracted from the crucible, some foils with a relatively large surface (several mm^2) and a thickness of about 100–200 μm were directly selected for the measurements. In particular, a large single crystalline foil with a surface of almost 1 cm^2 was used for most of the temperature dependent measurements.

Some other samples were prepared from rhombohedrical single crystals (about $1\times 1\times 5$ mm^3) thinned down to 40–60 μm and then mechanically polished with diamond powder. A very small single crystal 150 μm thick, with two natural, opposite and perfectly parallel facets, was used to measure the transmittance from 0.05 up to 0.6 eV, with the help of a microscope mounted on a Fourier transform spectrometer (Bruker IFS113v).

Transmittance (T) and reflectance (R) measurements were performed in the energy range 0.5–1.7 eV, with a spectrophotometer Varian mod. Cary 5 and with a spectral resolution of about 10 meV. An aluminum mirror, whose absolute reflectivity had been independently determined, was used as a reference for R measurements.

For the low temperature measurements, the samples were placed on the cold finger of a flux cryostat using hydrogen and helium gas. The temperature was monitored by a thermocouple placed in the vicinity of the sample. In order to avoid and eliminate eventual spurious effects due to the cryostat window and to obtain an absolute evaluation of the absorption coefficient, we carefully measured T and R at room temperature with and without the cryostat. Unfortunately, due to the small dimensions of the samples and the difficulties to have perfectly parallel planar surfaces, a loss of signal can occur and this could be different in the different samples.

III. RESULTS AND DATA ANALYSIS

R and T spectra at room temperature of the largest ($S1$) and the thinnest ($S2$) samples are shown in Fig. 1. We notice that transmittances are different for the different samples, but no defined correlation with the thickness can be found. Moreover, similar differences are observed among the reflectance measurements, too. Since no effects, due to the orientation of the samples, were detected by measurements with polarized light below 1.5 eV, the main origin of such discrepancies among the different samples in the measured intensities are geometrical effects, due to the roughness and the nonparallelism of the surfaces.

The occurrence of such effects at the surfaces prevents the direct determination of the optical functions, in particular, of the absorption coefficient, from the measured data. In order to bypass this difficulty, we considered the multiple reflection contributions of light inside a layer and we introduced two parameters, c_1 and c_2, taken constant in the energy range investigated and ranging between 0 and 1, to quote the roughness and the surfaces parallelism, respectively,

$$R = c_1 R_0 + c_1^3 c_2 (1 - R_0)^2 R_0 e^{-2\alpha x} + \cdots , \tag{1a}$$

$$T = c_1^2 c_2 (1 - R_0)^2 e^{-\alpha x} + c_1^4 c_2^2 (1 - R_0)^2 R_0^2 e^{-3\alpha x} + \cdots . \tag{1b}$$

With such a rough modelization, we were able to determine from the experimental R and T and for every sample the reflectivity R_0 and the absorption coefficient α (x is the sample thickness as determined by an optical microscope within an error of a few μm).

Three criteria guide such a way of proceeding and permit a reliable evaluation of the results: (i) having negligible polarization effects, the reflectivities obtained for the different samples should be equal as far as possible; (ii) these reflectivities must coincide with the independently measured bulk reflectivity, which increases monotonically from 0.19 at 0.5 eV up to 0.23 at 1.5 eV; (iii) the transmittance of an ideal sample ($c_1 = c_2 = 1$) must agree with the measured one with the IR microscope, which attains the value of about 0.7 at 0.6 eV (consistent with the above mentioned reflectivity and $\alpha = 0$).

Our results well accomplish these three conditions giving a spectral dependence of the absorption coefficient as shown in Fig. 2 for $S1$ and $S2$ samples. The remaining small differences between the absorption of the two samples could be ascribed to a different crystallographic orientation of the surfaces (anisotropy effects) or to small changes, due to the different history and treatment of the samples, as well as to the coarseness of the used model.

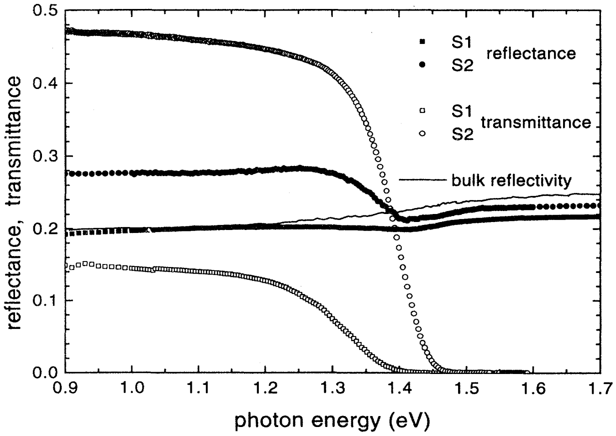

FIG. 1. Reflectance and transmittance at room temperature of the two samples $S1$ and $S2$, $\sim$ 200 μm and $\sim$ 60 μm thick, respectively. The line is the bulk reflectivity measured on a polished surface of a thick monocrystal.

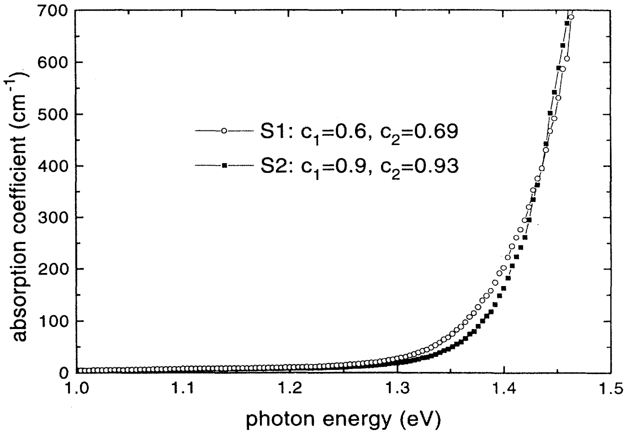

FIG. 2. Absorption coefficient obtained for the two samples $S1$ and $S2$. The different fractions of light lost for diffusion and nonparallelism of the surfaces are given by $(1-c_1)$ and $(1-c_2)$, respectively.

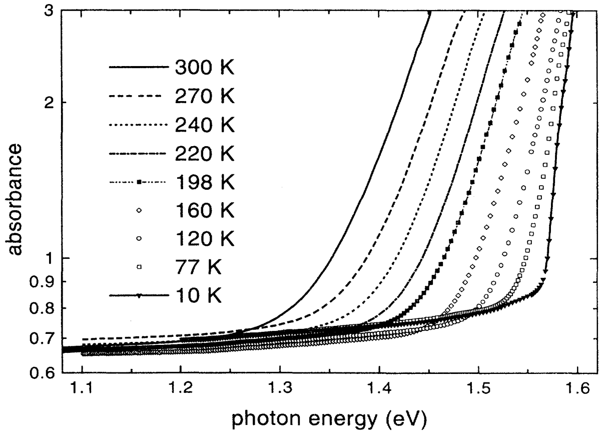

FIG. 3. Absorbance of the sample $S1$ at the absorption edge as a function of temperature.

Figure 3 shows the absorbance ($A = -\ln T$) results for the sample $S1$ at different temperatures from 10 K up to room temperature. One notices a relatively large blueshift of the absorption edge for decreasing temperatures.

IV. DISCUSSION

Apart from the determination of the absolute value, it is interesting to note that the spectral dependence of the absorption at the edge is not described by the usual dependence $A \propto (\omega - \omega_0)^x$, with $x = 0.5$ or 2 (for direct and indirect energy gap, respectively). A plot of log A vs log ω shows that x should range between 5 and 15, depending on the temperature. Anyway, three different spectral behaviors have been tested; $A \propto (\omega - \omega_0)^x$, $A \propto \exp[a(\omega - \omega_0)]$ and $A \propto \exp[a(\omega - \omega_0)^2]$.

The simple exponential (Urbach tail) gives a fairly good description of the data. The absorption edge ω_e can be easily determined as the point where the two linear behaviors in the plot of log A vs ω (as, e.g., in Fig. 3), below and above the change of slope, are crossing. The values of ω_e are independent of the sample investigated and have the temperature dependence illustrated in Fig. 4. The data of ω_e vs T behave like in the usual semiconductors and can be fitted by well-known formulas.[21] By using, e.g., the Lautenschlager formula $\omega_e(T) = \omega_g + a_g\{1 + 2/[\exp(\theta_g/T) + 1]\}$, one obtains the fit shown in Fig. 4, with the values $\omega_g = 1.67$ eV, $a_g = 0.10$ eV, and θ_g=202 K. $k\theta_g$ is the average energy of the phonons responsible, via electron-phonon coupling, of the shift of the energy gap itself.

The steepness parameter a in the exponential increase of the absorbance is temperature dependent, too (Fig. 4). According to the theory of the Urbach rule,[22] a follows a functional dependence $a(T) = (2\sigma/k\theta_0)\tanh(\theta_0/2T)$, where σ is an adimensional parameter of the order of unity and $k\theta_0$ represents an energy related to vibrational levels, which should, in principle, be equal to $k\theta_g$ (θ_0 = 162 K for the dashed line in Fig. 4).

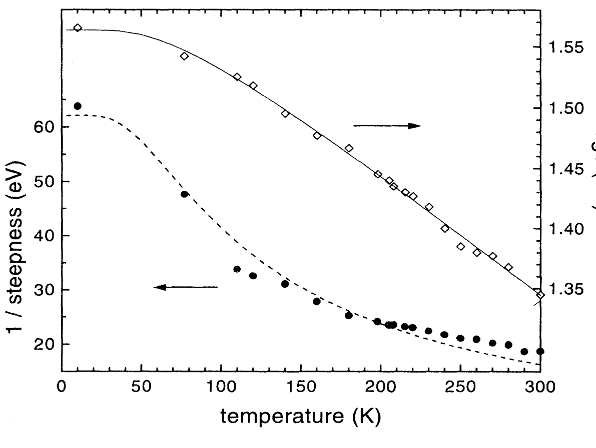

FIG. 4. Energy value and steepness parameter of the absorption edge of CuO as a function of temperature.

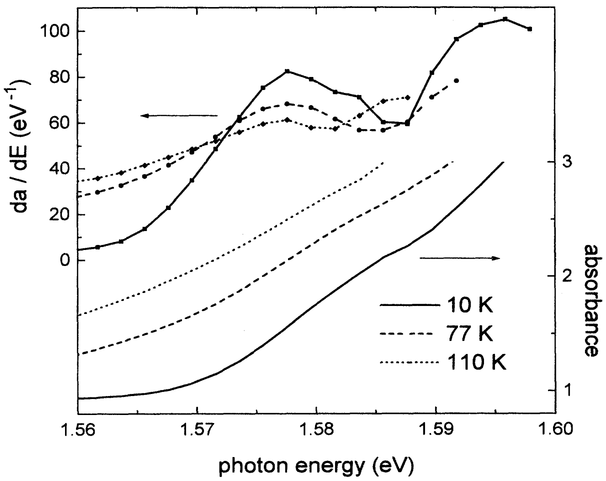

FIG. 5. Absorbance of the sample $S1$ and its first derivative at the lowest temperatures.

The appearance of Urbach tail in crystalline samples has been largely discussed in the literature and several models have been proposed to explain the origin of such a behavior.[22,23] Anyway, the major features which can be applied in the case of CuO are (i) a high ionicity; (ii) a steep increase of the density of states above the gap; and (iii) a local fluctuation of the gap value due to stress, change of interatomic distance, and/or microscopic electric field, related to the lattice vibrations (this implies a strong electron-phonon coupling). The energy distribution of such gap fluctuations is described by a Gaussian dependence.[22,23]

In effect, the best fit of the experimental absorbances above the absorption edge seems to be achieved by using a Gaussian type of spectral dependence instead of a simple (Urbach) exponential. Such a result, together with the confirmed ionicity of CuO (Ref. 24) and the small oscillator strength of the excitations across the gap (as deduced from ellipsometric and reflectivity results), supports the idea of narrow bands of quasilocalized states occurring in CuO.

Two further aspects have to be discussed. One is the occurrence of a change of slope in the absorption increase above the gap measured at the lowest temperatures. The effect is shown in Fig. 5, where the absorbance derivative is reported too. Such a behavior has been observed in several samples and is likely to be ascribed to excitonic structures emerging from the absorption tail.

The last remark concerns the effect of magnetic order on the absorption edge. No evident changes can be noticed in Fig. 4, even if small anomalies exist near 212 K and around 230 K (the two temperatures of the magnetic transitions). Anyway, it is interesting that such anomalies become more important and defined by considering the $\omega_e(T)$ and $a(T)$ obtained by a fit with Gaussian curves (whose area is kept constant). A direct connection of the absorption data with magnetic order remains an open question, but the indication exists of some effect of ordering on the optical data.

V. CONCLUSIONS

The optical response of CuO around the absorption edge has been investigated and an estimate of the absorption coefficient has been done. The data show a very large temperature dependence of the absorption edge and Urbach tail behavior. This confirms a localized character of the states involved in the absorption processes (likely due to Cu *d* states) and suggests a strong coupling of the electronic states with the lattice.

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