Optical absorption spectra of nanocrystalline cupric oxide: possible effects of nanoscopic phase separation

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Abstract
Optical absorption spectra of nanocrystalline cupric oxide CuO samples, obtained using the converging spherical shock wave procedure, reveal significant spectral weight red-shift as compared with spectra of single-crystalline CuO samples. In addition, some of these samples manifest remarkable temperature-dependent resonances near 1.3–1.6 eV. The minimal model suggested to explain both effects implies the CuO nanoceramic to be a metastable system of metallic-like nanoscale droplets with Drude optical response, nucleating in the bare insulating medium under the stimulating influence of the conditions of the specimen treatment. Simple effective medium theory is shown to provide a reasonable description of the experimental spectra in terms of the plasmon features due to the droplet phase.

1. Introduction

In the past decade there has been a good deal of renewed interest in the cupric oxide CuO, generally recognized as the prototype material of a broad family of strongly correlated (SC) oxides. At present, the paramount role of various inhomogeneities in the formation of the unconventional physical properties of these systems is becoming increasingly clear, and the tendency toward electronic phase separation is recognized as their generic feature. The stripe scenario has gained prime importance in this context, and the observation of stripes in a representative set of HTSCs and non-superconducting oxides, including CuO [1], was reported.

While the nature and the actual existence of this *intrinsic* inhomogeneity in SC oxides remain hotly debated issues, there are a number of experimental techniques for inducing the electronic inhomogeneity extrinsically. In this connection, the catalytic properties of CuO in certain chemical processes are noteworthy [2]; they indicate its liability to form metastable

states. Hence, studies of CuO, subject to various external perturbations, capable of inducing the nucleation of the novel phases in the parent matrix, are of significant importance.

Investigations of such a controllable *extrinsic* inhomogeneity may shed light on the phase separation phenomena in doped SC oxides and offer a unique opportunity to get insight into the underlying physics of these systems in a direct way. Below, we present the results of optical studies of a series of high density polydisperse CuO nanoceramics. This nanocrystal material belongs to the metastable highly imperfect system of compounds that are likely to exhibit a strong spatial non-uniformity with a broad spread of concentration and physical properties of the inhomogeneities. The absorption coefficient spectra of the samples, measured in the range 1–3 eV, displays a remarkable red-shift as compared with the corresponding spectra of nominally pure stoichiometric CuO single crystals [3]. In addition, a peculiar fine oscillating structure with an unconventional temperature dependence is resolved near 1.3–1.6 eV. In general, these findings are very similar to the results obtained earlier on, in the course of detailed studies of single-crystalline CuO samples exposed to a fluence of fast electrons, neutrons and nitrogen ions [4–6]. The similarity of the optical spectra in the two cases makes it possible to draw the important conclusion that the stability of the parent dielectric phase of these oxides can be easily suppressed, and to speak of some 'defect phase' with an enhanced low energy optical response, that may start to nucleate under rather general conditions.

2. Experiment

The CuO nanoceramics were prepared by processing standard polycrystalline samples with the mean size of the grains varying from 5 to 20 μm [7], using converging spherical shock waves [8]. The procedure has been implemented with samples sealed in the hermetically sealed steel container, which prevented their contamination from the environment. Highly compressed CuO nanoceramics, with a density that amounts to 99% of that of the theoretical close-packed structure, were thus obtained, the mean size of the grains varying from 20 to 100 nm depending on their distance from the core of the compressed spherical specimen [7].

The optical studies were performed with three platelets of 40–70 μm thickness, henceforth denoted as Nos 1, 2 and 3, with the mean size of the grains equal to 20, 60 and 100 nm, respectively, cut from the bulk specimen, the granularity being estimated using a scanning tunnel microscope and by analysis of the broadening of the x-ray diffraction lines (XRD). The XRD data and the analysis of the O Kα x-ray emission spectra (XES) showed that all samples were single phase [9]. The annihilation radiation angular correlation (ACAR) analysis gave evidence of a considerable concentration of the oxygen vacancies and their agglomerates at the boundaries of the crystallites [10]. The measured absorption spectra $K(\omega)$ are shown in figure 1, where the data are given in units of the absorption coefficient of sample 3 at 2.0 eV. It can be seen that the spectra of the nanogranular samples differ in many respects from that of CuO single crystal (see figure 1(B)). To be noted is a significant broadening of the fundamental band edge and the dramatic transfer of the spectral weight to lower energies as compared to the single-crystalline CuO case, where the fundamental band edge is distinctly observed at 1.45 eV [3]. Similar effects that are reminiscent of those observed for underdoped HTSCs [11] have been previously reported in the spectra of CuO single crystals after fast particle bombardment [4–6].

The most striking peculiarity of the spectra (figure 1) is a fine oscillating structure, smooth or quite pronounced, that emerges near the fundamental band edge. This is most clearly observed in the spectrum of sample 2, where there is a remarkable 'peak–dip–hump' feature with three peaks resolved at 1.33, 1.55 and 1.82 eV. This feature manifests a puzzling temperature dependence, most distinctly observed in the spectrum of sample 2 (figure 1(C)):
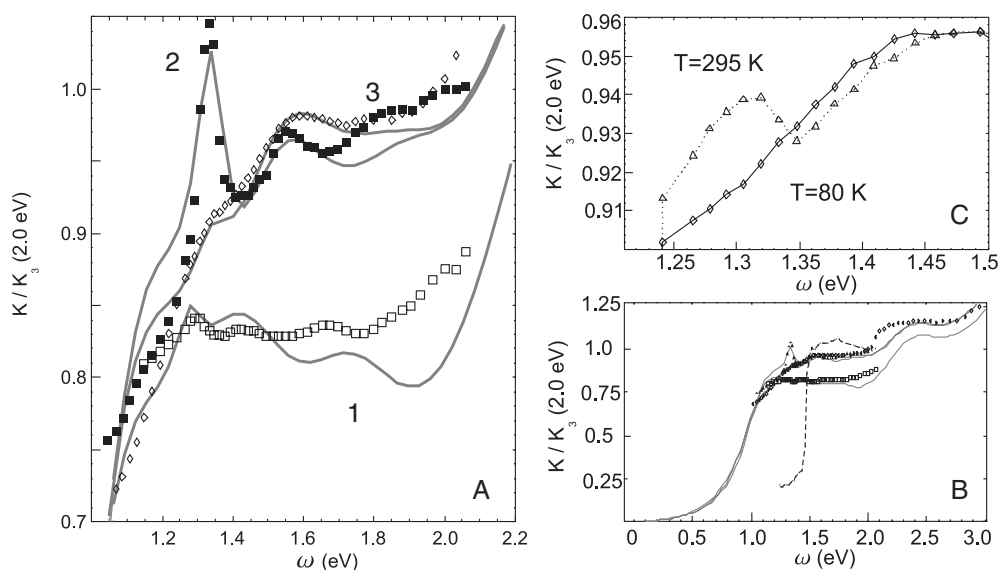
Figure 1. (A) Normalized room temperature absorption spectra of three CuO samples. Solid curves are the effective medium theory fits (see the text for details). (B) The overall evolution of the spectra over the whole range considered. The dashed curve marks the fundamental absorption band edge of pure CuO single crystal [4]. (C) A fragment of the spectrum of sample 2, measured at two temperatures.

while clearly resolved at $T = 295$ K, it completely disappears upon cooling to 80 K. This behaviour is obviously incompatible with the excitonic picture. Some discrepancies in the sample 2 spectra as observed in figures 1(A) and (C) are related to the use of the cryostat required for the low temperature measurements that entails an increase of optical loss and, correspondingly, an increase of the optical slit of the monochromator, resulting in the smearing of the absorption spectra (figure 1(B)) and a significant loss of resolution.

While the shape of the spectral profile (figure 1(A)) is ascertained with high precision, it is hard to display the absolute value of the absorption as reliably. For example, the intensity of the pronounced peak at 1.33 eV in the spectrum of sample 2 is found to be about $2100 \, \text{cm}^{-1}$. This value is in reasonable agreement with the earlier reported absorption coefficient of the CuO polycrystals [12]. On the other hand, so small an absorption near the fundamental band edge is at variance with the values derived from the complex dielectric permittivity of insulating cuprates such as La_2CuO_4, from where the values of $K \sim 10^5 \, \text{cm}^{-1}$ can be obtained [11]. We believe that such a discrepancy is primarily related to the differences of the techniques, based either on transmittance or reflectance analysis. While unimportant for an ideal uniform medium, it may become crucial and unavoidable for strongly disordered systems, where the surface and bulk properties of the sample can differ due to the variation of the concentration and the structure of the inhomogeneity. In fact, it is only possible to speak of the effective optical characteristics of an inhomogeneous system, where the 'physical' contribution, related to the energy band structure, can hardly be separated from the 'geometrical' one, which reflects the subtleties of the nanoscale structure of a particular sample. Thus, for example, it is difficult to derive the dielectric permittivity of strongly inhomogeneous film from measurements of its optical density, because the effective optical path length can be strongly elongated due to multiple reflections accompanied by an intricate frequency dependence.
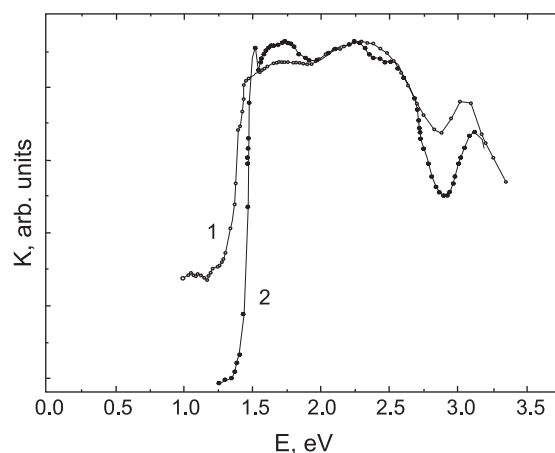
Figure 2. The fundamental absorption edge in the nanocrystalline CuO sample annealed at 900 °C (2) as compared with that of the pure single-crystalline CuO sample (1) [4].

3. Discussion

Now look at figure 1, where the results of the present study are summarized. To be noted first is the substantial red-shift and the broadening of the fundamental absorption edge. Taking into account the good chemical purity of the samples, we can speculate that the anomalous spectral weight red-shift evidences the nucleation of some highly polarizable phase with a pronounced low energy optical response, induced by the extremal conditions of the sample preparation. Indeed, the optical spectra of the systems with nanoscale inhomogeneities are known to exhibit the specific sharp features, the so-called surface plasmon resonances (SPR). These are most often observed in the spectra of artificially sintered composites that consist of dielectric matrices with metallic nanoparticles, such as $50BaO–50P_2O_5$ glass or Al_2O_3 matrix with silver embeddings [13, 14]. However, in the present case of CuO nanoceramic, we argue that we are dealing with the nucleation of metal-like droplets due to the clustering of inherent defects, since contamination of the samples within the hermetically sealed container is ruled out. This process, caused by the nanocrystalline structure of the samples, may be favoured by the inherent tendency of the strongly correlated oxides toward phase separation. The annealing experiments make it possible to convincingly discriminate between the internal phase separation and some extrinsic contamination as possible sources of the observed spectral features of the CuO nanoceramics, in favour of the former. The annealing of the CuO samples at 900 °C leads to removal of the enhanced low energy spectral weight and restores the fundamental absorption spectra to their original shape, typical of pure CuO single crystal (see figure 2). From the structural point of view, the annealing results in a drastic reduction of the oxygen vacancy concentration and in the growth of the crystallites up to micron sizes [10], while the density of the ceramics remains high (almost 96%).

Thus, to formulate a simple semi-qualitative model of such a phase non-uniformity [15], we assume the nanoceramic CuO samples to form a disordered insulating matrix with metallic-like inclusions (droplets). Hereafter, this assumption will be proven reasonable although, strictly speaking, the character of the optical response of the novel phase near zero frequency and its dc conduction properties cannot be fixed from the available experimental data. Note, however, that the room temperature dc resistance of the nanoceramics is about 10^4 Ω cm and its temperature dependence shows distinctly an activation character that attests unambiguously to the whole samples being insulating.

The optical properties of such metal–insulator composites are most often described within effective medium theories (EMT), which replace the physical characteristics of the composite with their mean-field quantities. Thus, in the present study, our analysis of the spectra of CuO nanoceramic is based on the following expression for the absorption coefficient:

$$K(\omega) = 2\frac{\omega}{c}\,\mathrm{Im}\,\sqrt{\varepsilon_{\mathrm{eff}}(\omega)}, \tag{1}$$

where the effective dielectric permittivity $\varepsilon_{\mathrm{eff}}$ has been calculated using the familiar Maxwell-Garnett approximation [16], widely applied in the description of heterogeneous systems with the so-called 'cermet topology', where the inclusions are completely surrounded by the host medium [17]. It yields the following expression for $\varepsilon_{\mathrm{eff}}$:

$$\varepsilon_{\mathrm{eff}} = \frac{(1-p)\varepsilon_{\mathrm{d}} + \sum_i \Delta_i \varepsilon_i}{(1-p) + \sum_i \Delta_i}, \tag{2}$$

where

$$\Delta_i = \left\langle \frac{\varepsilon_i}{\varepsilon_{\mathrm{d}} + L^{\langle i \rangle}(\varepsilon_i - \varepsilon_{\mathrm{d}})} \right\rangle. \tag{3}$$

Here ε_{d} denotes the dielectric permittivity of the bare dielectric CuO medium, $\langle \cdots \rangle$ stands for the averaging over the inhomogeneity, including the distribution of the volume fractions p_i, orientations and other parameters pertaining to different species of embeddings with dielectric permittivities ε_i, and the principal values of the depolarization tensors are denoted by L s, the overall concentration of inclusions being p. Thus, for a discrete set of species of randomly oriented embeddings,

$$\Delta_i = \frac{p_i}{3}\sum_{j=1}^{3}\frac{\varepsilon_i}{\varepsilon_{\mathrm{d}} + L_j^{\langle i \rangle}(\varepsilon_i - \varepsilon_{\mathrm{d}})}, \qquad \sum_i p_i = p, \tag{4}$$

where j runs over the three depolarization factors of the grains of the ith species.

To simplify the analysis, we described the droplets of the novel phase using the usual Drude expression:

$$\varepsilon_i = 1 - \frac{\Omega_{\mathrm{p},i}^2}{\omega^2 + \mathrm{i}\omega\gamma_i}, \tag{5}$$

where Ω_{p} and γ are the *effective* plasma frequency and the damping constant, respectively. As for the dielectric CuO medium, within the spectral range considered we simulated its dielectric permittivity with the superposition of two Lorentz contributions:

$$\varepsilon_{\mathrm{d}} = \varepsilon_\infty + \frac{1}{\pi}\sum_{k=1,2}\frac{I_k}{\omega_k^2 - \omega^2 - \mathrm{i}\gamma_k\omega}, \tag{6}$$

centred at $\hbar\omega_1 = 2.35$ eV ($\gamma_1 = 0.9$ eV, $I_1 = 14.256$) and $\hbar\omega_2 = 4.5$ eV ($\gamma_2 = 0.9$ eV, $I_1 = 469.8$), where I_k and γ_k are the strength and the damping factor of the kth oscillator, respectively, and $\varepsilon_\infty = 3.5$.

The free parameters of the model are those of the Drude formula, equation (5), the volume fraction p of the droplets and their geometric shape, which enters EMT via the depolarization factors. Following the commonly accepted approximation, we assumed the droplet to be ellipsoidal, with the ratios of the two semi-axes to the third one denoted as α and β, respectively. Within this approach these quantities cannot be ascertained at a microscopic level, but should be determined from comparison with experiment. Thus, choosing $p \approx 20\%$, $\Omega_{\mathrm{p}} \approx 4.5$ eV, $\gamma \approx 0.5$ eV, $\alpha \approx 0.7$, $\beta \approx 1.6$ we arrive at a reasonable description of the spectra of all the samples excluding the 'peak–dip–hump' feature revealed for sample 2.
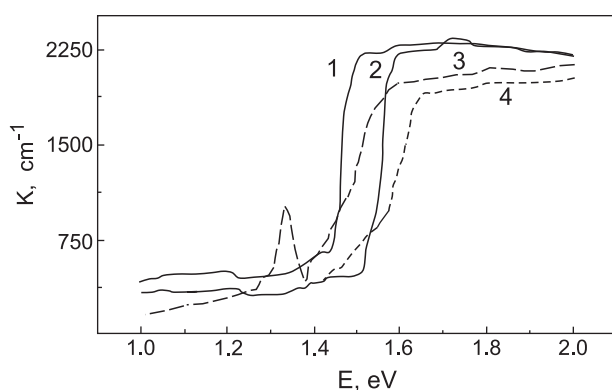
Figure 3. The absorption spectra of the CuO single crystal before (curves 1, 2) and after (curves 3, 4) the fast electron bombardment, measured at 300 K (1, 3) and at 80 K (2, 4). Note a peculiar sharp feature near 1.3 eV clearly visible in curve 3. The data are reproduced from [4].

Table 1. Fit parameters for the metallic-like droplets for the samples Nos 1–3.

No	p_1	$\Omega_p^{(1)}$ (eV)	$\gamma^{(1)}$ (eV)	α_1	β_1	p_2	$\Omega_p^{(2)}$ (eV)	$\gamma^{(2)}$ (eV)	α_2	β_2
1	0.186	4.35	0.45	0.72	1.45	0.0265	4.25	0.02	1.6	1.6
2	0.201	4.75	0.5	0.73	1.6	0.0084	4.75	0.01	1.9	1.9
3	0.20	4.75	0.5	0.73	1.6	0.0042	4.75	0.07	1.9	1.9

Proceeding to the discussion of the latter experimental finding, it is worthwhile noting that a similar feature was found earlier in the absorption spectra of pure CuO single crystal after electron irradiation [4], reproduced in figure 3, together with the spectrum of the non-irradiated CuO sample. It may be seen that besides a slight broadening of the absorption edge, the bombardment leads to the emergence of a peculiar sharp feature near 1.3 eV that cannot be ascribed to either of the known optical excitations of the parent CuO monoxide. Furthermore, the feature, clearly visible at room temperature, disappears with the lowering of the temperature to 80 K—in other words, revealing behaviour as for nanocrystalline sample 2.

In our opinion, the existence of rather narrow spectral features, strongly marked in the spectra of both nanocrystalline sample 2 and irradiated single crystals, points to a sizable volume fraction of droplets with fairly 'good' metallic properties, or a small magnitude of the Drude damping parameter γ. Among its most probable origins, we consider e.g. the precipitation of Cu nanograins. Indeed, a macroscopic concentration of Cu has been previously found in cupric oxide after fast nitrogen ion bombardment [6] and plastic deformation [18].

To fit the fine resonant structure, more or less clearly discernible in the spectra of all the samples, we introduced a simple distribution of the inhomogeneity structure by considering two species of droplets with volume fractions $p_1 \gg p_2$ and damping parameters $\gamma_1 \gg \gamma_2$, or 'bad' and 'good' metal, respectively. The fitted parameters for all the samples are listed in table 1. The comparison of the theoretical curves with experiments shows that the resonant structure of the absorption spectra that evolves into the quite pronounced 'peak–dip–hump' feature in spectrum 2 can be naturally assigned to surface plasmon (Mie) resonances that are typical of systems with a nanoscale inhomogeneity. We note the striking sensitivity of the theoretical spectra to the variation of the parameters of the inhomogeneity, and especially to those of the phase with small damping constant. The slight changes in the relative volume fractions of

the two sorts of inclusions result in dramatic effects in the absorption spectra. This makes it possible to account reasonably well for the difference of the spectra of samples 2 and 3, because a subtle variation of the parameters from sample to sample is practically unavoidable. Such a variation of the internal texture of the inhomogeneity could be driven also by the temperature. It is clearly observed in panel B of figure 1, where a fragment of the absorption spectrum of sample 2 is depicted for two temperatures. It can be clearly seen that the pronounced peak at 1.33 eV in the room temperature spectrum completely disappears during cooling. Interestingly, the spectra of sample 2 measured at $T = 80$ K look quite similar to the room temperature spectra of samples 1 and 3. The effective medium approach makes it possible to reproduce the essential features of experimental spectra, slightly varying the model parameters. The effect of the temperature may be ascribed mainly to the changes in the relative volume of the second ('good') component. We have found that the reduction of the relative volume of the highly polarizable phase with lowering of the temperature by less than 8% is enough to simulate such singular temperature behaviour. The underlying mechanism of this volume fraction effect may be related, e.g., to the onset of 3D antiferromagnetic order in CuO, that takes place near $T \sim 230$ K. In general, the onset of antiferromagnetism at low temperatures is expected to entail suppression of the metallic-like phase. The way in which this occurs may be via the direct reduction of the volume fraction and/or changes in the properties of the droplet. Moreover, the volume effect can be accompanied also by a deformation of conducting inclusions that results in some shift and possible splitting of the geometric resonances, thus contributing to the broadening of the feature observed in the 295 K spectrum. We regard its unusual temperature dependence as an important signature of its 'geometric' nature.

In conclusion, the optical absorption of nanocrystalline CuO samples has been studied in spectral range 1–3 eV. We found a pronounced spectral weight red-shift as compared with the spectra of single-crystalline CuO samples, and fine spectral structure near 1.3–1.6 eV. The minimal model suggested to explain both effects implies the nanoceramic CuO to be a system of two species of metallic-like droplets with volume fractions $p_1 \gg p_2$ and damping parameters $\gamma_1 \gg \gamma_2$, respectively, dispersed in an effective insulating matrix. Theoretical analysis within the effective medium framework is shown to provide a good semi-quantitative interpretation of experimental findings in terms of the surface plasmon (Mie) resonances due to the small volume fraction of metallic-like nanoscale droplets with Drude optical response embedded in the bare insulating medium. Nevertheless, it is worth noting that this simple model approach sets aside some subtle effects typical for inhomogeneous media—for instance, the interference effects due to multiple reflections of light in the platelets, whose role deserves special attention.

We emphasize a clear similarity of the optical responses produced by the extrinsic nanoscale inhomogeneity created in different ways (a shock wave as in present study or, e.g., fast particle irradiation) and the intrinsic nanoscale inhomogeneity created by chemical doping in parent insulating cuprates. This supports the idea of generic instability of these SC oxides as regards phase separation and the nucleation of metallic-like phases.

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