The optical constants of natural and artificial cuprite by an ellipsometric method

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SUMMARY. Ellipsometric measurements in the spectral range 250-850 nm have been made on polished single crystals of natural cuprite from Namibia and of artificial cuprite grown by a total-oxidation method from pure copper. Derived values of the refractive indices, absorption coefficients, normal reflectances, and the complex dielectric constants for the two materials are all closely similar, suggesting that the stoichiometry and purity are essentially the same. Values of the absorption coefficient at the red end of the spectrum are inconsistent with the observed transparency of the crystals, and are compatible with a 10 nm surface oxidation film of cupric oxide. This study is part of a wider survey of the effects of doping and stoichiometry on the optical parameters of cuprite.

Sample preparation

THE natural cuprite was cut from a crystal fragment from the Onganja mine, Namibia, obtained from the British Museum (Natural History) (B.M. 1974, 411). The polished surface, about 20 mm × 10 mm, was shown to be of a single crystal by back-reflection Laue X-ray photographs. Small inclusions of malachite were removed by abrasion; the only other imperfections were some fine cracks, and a few cavities less than 0·5 mm diameter.

The artificial cuprite was obtained by the controlled total oxidation in air of a sheet of copper, 20 × 10 × 0·5 mm and 99·9999% purity. The copper sheet, supported on platinum wires in an alumina boat, was heated in a tube furnace to 1050 °C for three hours to complete oxidation and then to 1085 °C for a further twenty-four hours to encourage grain growth. The sample was cooled slowly to 700 °C in the furnace under a partial vacuum of 100 mm Hg, and then to room temperature under a higher vacuum of 0·1 mm Hg. This cooling procedure ensured that the specimen stayed within the cuprite field of the Cu-O phase diagram, and was free from strain (Schmidt-Whitley et al., 1974; Martinez-Clemente et al., 1976). The resulting material proved to be a single crystal, 0·8 mm thick.

The specimens were mounted in cold-setting polyester resin, and mechanically lapped on lead solder plates to an optically flat surface of 6 μm roughness. They were then polished by hand on nap cloths to 1 μm, and finally on silk to ¼ μm, using diamond paste. The resulting surfaces possessed mirror finishes, except for the imperfections on the natural sample mentioned above. Both specimens were cleaned ultrasonically, rinsed in distilled water and pure alcohol, and blow-dried. The ellipsometric measurements were made immediately, to avoid the effects of appreciable surface film formation.

Ellipsometric measurements

Ellipsometry is a technique whereby the change in the state of polarization of light caused by reflection is interpreted in terms of the properties of the reflecting surface, and its general principles have been described by Muller (1973). The measurements in the present study were made on an automatic ellipsometer, employing servo-driven Glan-Foucault polarizer and analyser prisms controlled by power oscillators and phase-sensitive detectors (Roberts and Meadows, 1974). In this system (fig. 1), the light from a xenon arc source is collimated, plane-polarized, and modulated by a Faraday cell before striking the sample. The reflected beam travels through a second Faraday cell and
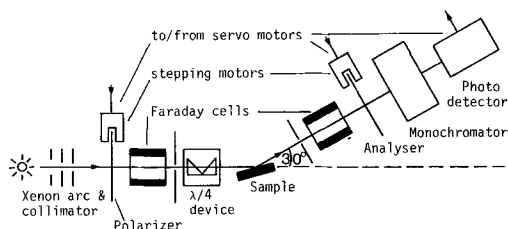

FIG. 1. Schematic layout of the automatic ellipsometer (see text).

TABLE I. *Ellipsometer parameters A and P (see text) at various wavelengths for freshly-polished natural and artificial cuprite, with computed values of* n, k, ε_1 ($= n^2 - k^2$), ε_2 ($= 2nk$), *and the normal reflectance* R.

Natural								Artificial							
λ (nm)	A	P	n	k	ε_1	ε_2	R_{calc} %	A	P	n	k	ε_1	ε_2	R_{calc} %	λ (nm)
250	18·78°	29·65°	1·70	1·61	0·32	5·47	31·10	18·47°	29·70°	1·68	1·62	0·20	5·43	31·44	250
270	19·71	31·59	1·83	1·71	0·42	6·26	33·06	19·01	31·39	1·76	1·72	0·15	6·06	33·41	270
290	21·57	34·67	2·08	1·84	0·95	7·68	35·46	21·02	34·07	2·02	1·83	0·72	7·36	35·15	290
300	23·22	35·65	2·26	1·82	1·80	8·25	35·20	22·63	35·04	2·19	1·82	1·50	7·95	34·98	300
315	24·93	35·58	2·41	1·73	2·82	8·31	33·98	24·44	34·88	2·34	1·71	2·54	8·02	33·57	315
325	25·26	35·59	2·44	1·71	3·03	8·31	33·79	24·81	35·02	2·38	1·70	2·76	8·09	33·50	325
340	25·87	37·60	2·57	1·78	3·44	9·11	35·31	25·42	36·98	2·50	1·77	3·13	8·87	35·03	340
355	27·77	40·28	2·84	1·76	4·94	10·02	36·38	27·34	39·74	2·78	1·78	4·58	9·86	36·23	355
365	29·29	41·13	2·99	1·67	6·17	10·00	36·10	28·90	40·66	2·94	1·69	5·81	9·93	35·99	365
400	33·30	39·96	3·22	1·27	8·77	8·15	33·65	33·15	39·44	3·19	1·27	8·58	8·09	33·41	400
440	35·84	38·21	3·32	0·99	10·04	6·54	32·34	35·64	37·30	3·28	0·99	9·77	6·47	31·98	440
470	37·86	35·32	3·36	0·74	10·76	5·01	31·34	37·57	34·74	3·33	0·76	10·52	5·08	31·11	470
500	39·21	30·00	3·35	0·55	10·91	3·65	30·26	38·84	29·44	3·31	0·57	10·64	3·76	29·96	500
540	39·73	17·71	3·23	0·32	10·33	2·05	28·20	39·58	18·48	3·22	0·34	10·28	2·18	28·19	540
580	38·79	9·71	3·08	0·20	9·45	1·26	26·19	38·62	10·16	3·07	0·22	9·37	1·33	26·05	580
600	38·23	7·58	3·02	0·17	9·07	1·03	25·34	38·08	8·32	3·01	0·19	9·00	1·14	25·25	600
650	37·20	5·41	2·91	0·14	8·45	0·79	23·97	37·06	6·20	2·90	0·16	8·39	0·91	23·88	650
700	36·57	4·43	2·85	0·12	8·11	0·67	23·16	36·41	5·26	2·84	0·14	8·04	0·80	23·04	700
750	36·13	3·84	2·81	0·11	7·87	0·60	22·60	35·93	4·68	2·79	0·13	7·78	0·73	22·44	750
800	35·82	3·47	2·78	0·10	7·71	0·55	22·22	35·58	4·18	2·76	0·12	7·60	0·66	21·99	800
850	35·61	3·12	2·76	0·09	7·61	0·49	21·95	35·28	4·16	2·73	0·12	7·46	0·67	21·64	850

the analyser before passing to the monochromator and photodetector. A 3-reflection coated quarter-wave device (Clapham *et al.*, 1969) compensates the circular component of the sample-induced ellipticity. The polarizer and analyser are kept at the null positions by stepping servo-motors controlled by signals from the detector unit. The system has a spectral bandwidth of 10 nm, and an angular resolution (of the polarizer and analyser positions) of 0·01°. The angle of incidence on the sample is held constant at 75°.

After aligning the instrument, the samples were mounted and the null positions of the polarizer and analyser recorded at 5 nm intervals for spectral scans from 250 to 850 nm. Light scattered from the surface imperfections of the natural cuprite specimen did not affect the main beam reaching the photodetector.

Results and discussion

The spectral values of the components of the complex index (refractive index, n, and absorption coefficient, k), complex dielectric constant (ε_1 and ε_2), and normal reflectance (R_{calc}) were calculated on the assumption that there was no surface film, using $n_0 = 1·000$ as the ambient (air) refractive index. The calculations were carried out on a DEC System 10 computer, using a program written by K. McC. Clarke (Ph.D. thesis, not yet published). The spectral curves are shown in figs. 2, 3, and 4 and a shortened list of numerical values is given in Table I. The C.I.E. colour coordinates were also calculated for the C.I.E. standard illuminant C, using the same program, and are shown in Table II.

Calculation of n and k may also be carried out using the equations given by Muller (1974, p. 183). The angular positions of the polarizer and analyser (Table I), for this ellipsometer system, are related to

TABLE II. *CIE chromaticity coordinates (Illuminant C, normal reflectance)*

Cuprite	x	y	Luminance	λ^*	Saturation
Natural	0·2894	0·2995	27·4059	480·3	9·3488
Artificial	0·2899	0·3005	27·3057	480·6	9·0769

* Dominant wavelength, nm.

the phase-difference (Δ) and amplitude-ratio (tan ψ) of the p and s components of the induced ellipticity by the equations $\Delta = 2P°$ and $\psi = 45° - A°$.

The main features of the reflectance spectra (fig. 2) are the two maxima at 290 nm (4·27 eV) and 360 nm (3·44 eV).[1] The positions of these maxima correspond well with calculations made by Dahl (1966), and with results obtained by Shestatskii et al. (1969) and by Gross et al. (1962), both of whom attribute the peaks to direct allowed transition from the Cu(3^d) valence bands to the conduction band. Gross et al. suggest that the transitions are excitonic in nature.
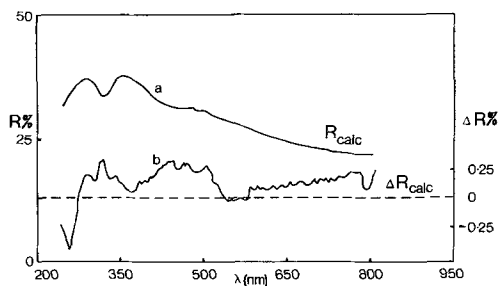
FIG. 2. Spectral reflectance curve for natural cuprite (above) and difference plot $R_{nat} - R_{art}$ (below, and r.h. ordinate).

The band-gap energy (Eg) was calculated from spectral values of ε_2 between 2·6 eV (477 nm) and 3·0 eV (413 nm). This region (figs. 3 and 4) is part of the fundamental absorption edge, but is not in the region of strong excitonic absorption (> 3·2 eV; < 387 nm), and may be attributed to the main inter-band transitions. Assuming that a linear relationship of the form $(\varepsilon_2/\lambda)^2 = A^2(hv - Eg)$ exists in this region (Gross et al., 1962), a value $Eg = 2·45$ eV was found. This figure is in agreement with the value 2·38 eV predicted by Zhilich and Makarov (1960) from theoretical calculations.

Cuprite is transparent at the red end of the spectrum (> 630 nm), with an estimated k of the order of 10^{-5} or less, so that the calculated values 0·14 to 0·09 in this region are anomalously high. The most probable cause is a relatively opaque surface film, and there are indications that such a film has developed even in the short time between polishing and measurement. The simplest assumption is that oxidation to CuO is involved, and on this basis 'pseudo-k' values were computed for cupric oxide films of various thicknesses. Published values of n and k for cupric oxide were used (Ladelfe et al., 1972), with a zero value of k for the cuprite substrate. A cupric oxide film approximately 10 nm
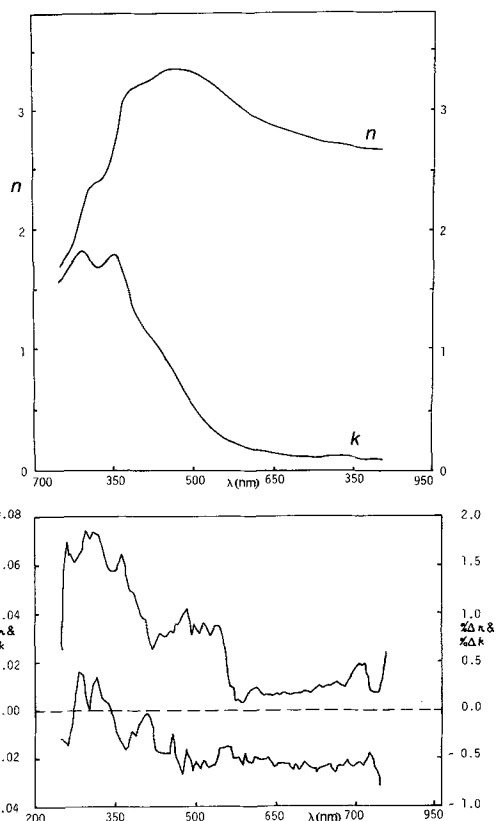
[1] Energy (in eV) × wavelength (in nm) = 1239·919.

FIG. 3a (top). Spectral dispersion of n and k for natural cuprite. b (bottom). Difference plots ($n_{nat} - n_{art}$) and ($k_{nat} - k_{art}$). Absolute differences (l.h. ordinate) and relative differences (r.h. ordinate).
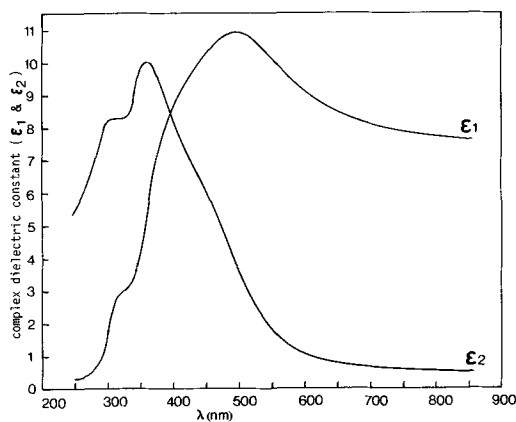

FIG. 4. Spectral dispersion of the complex dielectric coefficient (ε_1 and ε_2) of natural cuprite.

thick would account for the anomalous k values, and have minimal effect on the observed transparency. Further experiments are planned to examine the surface film in greater detail.

The spectra of these samples of natural and artificial cuprite are remarkably similar, despite their difference in origin. The calculated normal reflectances differ by less than 0·5%, and the refractive indices by less than 2% between 250 and 500 nm and 1% between 500 and 850 nm. This indicates that, although the natural specimen contained inclusions of malachite, the cuprite phase in the area covered by the ellipsometer light beam (about 15 × 2 mm) is relatively pure. Both specimens were examined using an AQD energy dispersion analyser, and showed less than 0·05% of any impurity. The results also suggest that the stoichiometry of the two specimens is essentially the same.

Further work is planned to assess the effects of non-stoichiometry in cuprite, induced by higher oxygen pressures and by doping the material with various cations.

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