Optical constants of Cu, Ag, and Au revisited

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Abstract

We have determined the optical constants in the energy range 0.1-6 eV for bulk Cu, Ag, and Au using Kramers-Kronig analysis of previously unpublished reflectance data. The results are compared to those commonly used from the literature.

Studies of the optical properties of the transition metals culminated in 1981 in a two volume set of figures and tables [1, 2]. These volumes have gone out of print but the data were abridged and published in the Handbook of Chemistry and Physics [3]. The originals have also been scanned and are available on one of the authors' websites [4]. Other authors also compiled data sets, including the well known volumes by Palik [5] which included the transition metal data. To our knowledge, there have been no more recent experimental studies, such work having gone out of vogue as investigations of the band structure through photon spectroscopies have yielded to photoemission and related spectroscopies that probe E(k) with exquisite precision.

The optical constants of the noble metals Cu, Ag, and Au are important to those who use the data for such studies as photonics, plasmonics and nanoparticle arrays [6]. While the optical constants in Ref. 2 have stood the tests of time for Au, those for Cu and Ag were taken from tabulations by Hagemann, Gudat, and Kunz (HGK) [7, 8] who in turn relied on the results by Johnson and Christy (JC) [9]. To provide a critical reassessment of the optical properties of Cu and Ag, we returned to some largely unpublished absorptivity measurements by Weaver et al. While the reflectance results were shown in Ref. 2, the authors were interested at that time in structure in the dielectric constants and those structures were well described by JC [9] (see the comparison figures in Ref. 2). Here, we are interested in the magnitudes of ε and N, the complex dielectric constant and complex index of refraction, and we performed Kramers-Kronig analyses to compare with prior results in the 0.1-6 eV range. Extensive comparisons that extend to 30 eV are available from the Weaver website [4].

The samples were mechanically polished single crystals that were chemically cleaned to remove work damage, as described previously [1, 2]. The measured quantity was the absorptivity, A = 1-R where R is the reflectivity. In the infrared, R is nearly 100%, and a measurement of A rather than R provides inherently greater accuracy. For Ag, to extend the spectral range for the KK analyses, we used the results from Leveque, Olson, and Lynch to 30 eV [10] For Cu, we tied our results to those of JC [9] and then HGK to 30 eV. Standard power law extrapolations of the form $R = R_o E^{-3.5}$ were used to 1000 eV.

Figures 1-3 summarize the reflectances and Figs. 4-6 summarize the dielectric constants for Cu, Ag, and Au, using continuous lines for our results and appropriate symbols for JC, Palik (who reproduced the Cu data of Ref. [7, 8, 11]; the Ag data of Ref. [10, 11, 12]; and the Au data of Ref. [11, 13, 14]) and HGK (who reproduced the Cu data of Ref. [9, 15]; and Ag and Au data of Ref. [9, 16]).

The JC dielectric constants have been widely used, in part because they were presented in tabular form but also because they became the basis for other tabulations. JC used reflection and transmission measurements on 185 – 500 Å thin-films evaporated onto fused quartz substrates. The evaporations were performed in an oil-pumped bell-jar system at pressures of 10^{-6} Torr. Much has been learned about the morphologies of such films, notably their polycrystalline form and the tendency to agglomerate. Such thin-films are often rough, inhomogeneous and far from bulk-like. Of the three metals, Ag would likely be the most bulk-like because of the low barriers for surface diffusion and Cu would be the least bulk-like because of diffusivities but also because of ambient atmosphere contamination at 10^{-6} Torr. In addition, transmission/reflection methods are inherently sensitive to the final film surface morphology. As a consequence, there is large uncertainty in the measured JC optical constants, as those authors noted in Figs. 2, 3, and 4 of Ref. 9.

Kramers-Kronig analyses introduce uncertainties in the magnitudes of the dielectric constant, but those are minimized by measurements that scan the wide energy range of 0.1-30 eV. For that reason, and because our samples were single crystals, we suggest that the results of Figs. 4-6 are more representative of the metals than the thin film data. Although analysis of our reflectance data does not yield new structure in the dielectric constant, as expected, the magnitudes of those constants are quite different from those of JC. For example, the infrared values for ε_2 are lower by a factor of 2-4 for Cu where the greatest departure from bulk-like character is expected. The agreement is much better for Ag, for reasons mentioned above, and intermediate for Au. That said, many of those who are preparing samples by vacuum evaporation are using conditions that are not much different from those of JC. We leave it for them to assess their results in the context of the optical constants presented here and those available elsewhere [4].

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Table 1. Optical constants for Cu, Ag and Au

	Cu			Ag			Au		
E (eV)	R	ε_1	ε_2	R	ε_1	ε_2	R	ε_1	ε_2
0.10	0.994	-7180.10	1911.20	0.997	-7461.30	878.91	0.995	-6991.50	1507.60
0.15	0.994	-3410.30	601.93	0.996	-3557.80	385.58	0.995	-3173.20	453.84
0.20	0.994	-1957.60	263.71	0.996	-2045.30	167.58	0.995	-1795.60	192.16
0.25	0.994	-1265.20	137.08	0.996	-1321.50	89.36	0.995	-1150.60	98.35
0.30	0.994	-881.95	79.30	0.996	-921.87	52.04	0.995	-797.94	56.74
0.35	0.994	-648.36	49.85	0.996	-678.29	33.28	0.995	-585.08	35.61
0.40	0.994	-495.91	33.39	0.996	-519.61	22.62	0.995	-444.42	23.58
0.45	0.994	-391.07	23.48	0.996	-410.43	16.09	0.994	-350.20	19.82
0.50	0.994	-315.94	17.12	0.996	-332.14	11.87	0.994	-284.22	14.49
0.55	0.994	-260.24	12.83	0.996	-274.11	9.02	0.994	-234.07	10.84
0.60	0.994	-217.80	9.84	0.996	-229.91	7.02	0.994	-195.87	8.30
0.65	0.994	-184.71	7.71	0.996	-195.46	5.56	0.994	-165.98	6.48
0.70	0.994	-158.43	6.14	0.996	-168.08	4.50	0.994	-142.26	5.15
0.75	0.994	-137.21	4.98	0.996	-145.98	3.73	0.994	-122.75	4.13
0.80	0.994	-119.82	4.08	0.996	-127.90	3.14	0.993	-107.13	3.93
0.85	0.994	-105.40	3.38	0.996	-112.92	2.67	0.993	-94.43	3.26
0.90	0.994	-93.30	2.83	0.996	-100.34	2.29	0.993	-83.54	2.72
0.95	0.994	-83.04	2.40	0.995	-89.71	2.00	0.993	-74.17	2.28
1.00	0.994	-74.28	2.05	0.995	-80.64	1.76	0.992	-66.27	2.20
1.10	0.994	-60.16	1.52	0.995	-66.06	1.37	0.992	-53.74	1.61
1.20	0.993	-49.38	1.18	0.995	-54.93	1.08	0.991	-43.98	1.35
1.30	0.993	-40.96	0.94	0.995	-46.26	0.89	0.990	-36.45	1.14
1.40	0.993	-34.22	0.78	0.994	-39.38	0.74	0.989	-30.43	0.96
1.50	0.992	-28.74	0.67	0.994	-33.80	0.64	0.988	-25.50	0.81
1.60	0.991	-24.17	0.59	0.993	-29.25	0.57	0.986	-21.43	0.73
1.70	0.988	-20.31	0.58	0.992	-25.48	0.52	0.984	-17.99	0.65
1.80	0.984	-16.99	0.60	0.991	-22.32	0.48	0.979	-14.98	0.66
1.90	0.977	-14.12	0.66	0.991	-19.64	0.44	0.968	-12.44	0.77
2.00	0.970	-11.43	0.64	0.990	-17.34	0.40	0.953	-10.25	0.87
2.10	0.948	-8.50	0.74	0.988	-15.35	0.39	0.925	-8.26	1.05
2.20	0.745	-5.54	2.49	0.986	-13.64	0.37	0.880	-6.54	1.26
2.30	0.600	-4.88	4.69	0.985	-12.13	0.36	0.807	-4.95	1.48
2.40	0.590	-5.07	5.45	0.983	-10.81	0.34	0.647	-3.18	1.86
2.50	0.580	-4.92	5.57	0.981	-9.64	0.32	0.438	-1.92	2.79
2.60	0.570	-4.70	5.53	0.979	-8.58	0.31	0.331	-0.83	3.95
2.70	0.552	-4.31	5.44	0.976	-7.64	0.29	0.356	-0.89	5.06
2.80	0.532	-3.92	5.37	0.974	-6.78	0.27	0.368	-1.02	5.34
2.90	0.515	-3.60	5.31	0.971	-5.99	0.25	0.368	-0.94	5.54
3.00	0.495	-3.22	5.17	0.968	-5.25	0.23	0.369	-0.90	5.69
3.10	0.469	-2.78	5.15	0.963	-4.57	0.23	0.371	-0.92	5.77
3.20	0.453	-2.52	5.20	0.959	-3.92	0.20	0.368	-0.87	5.72

3.30	0.438	-2.27	5.13	0.944	-3.29	0.22	0.362	-0.76	5.68
3.40	0.421	-2.00	5.13	0.920	-2.70	0.25	0.356	-0.64	5.66
3.50	0.410	-1.81	5.14	0.875	-2.14	0.31	0.349	-0.49	5.65
3.60	0.400	-1.64	5.13	0.805	-1.59	0.36	0.346	-0.37	5.75
3.70	0.393	-1.53	5.10	0.700	-1.05	0.39	0.351	-0.38	5.93
3.80	0.384	-1.40	4.99	0.425	-0.33	0.40	0.360	-0.56	6.01
3.90	0.372	-1.22	4.92	0.065	0.52	0.80	0.366	-0.74	5.91
4.00	0.361	-1.04	4.87	0.090	1.17	1.66	0.369	-0.88	5.75
4.10	0.350	-0.86	4.83	0.146	1.19	2.52	0.368	-0.93	5.57
4.20	0.337	-0.63	4.84	0.191	0.87	3.08	0.367	-0.97	5.41
4.30	0.331	-0.46	4.98	0.217	0.57	3.31	0.368	-1.04	5.28
4.40	0.331	-0.39	5.12	0.235	0.35	3.44	0.370	-1.13	5.08
4.50	0.334	-0.37	5.25	0.249	0.15	3.48	0.370	-1.20	4.83
4.60	0.339	-0.42	5.38	0.256	0.03	3.46	0.364	-1.18	4.52
4.70	0.346	-0.51	5.48	0.263	-0.09	3.44	0.354	-1.08	4.28
4.80	0.355	-0.66	5.57	0.265	-0.15	3.37	0.344	-0.98	4.07
4.90	0.367	-0.90	5.61	0.267	-0.19	3.33	0.332	-0.86	3.88
5.00	0.379	-1.17	5.48	0.269	-0.24	3.27	0.319	-0.73	3.71
5.10	0.384	-1.33	5.31	0.269	-0.26	3.20	0.307	-0.61	3.59
5.20	0.392	-1.50	5.14	0.267	-0.27	3.13	0.295	-0.49	3.48
5.30	0.397	-1.63	4.90	0.265	-0.26	3.08	0.285	-0.40	3.39
5.40	0.400	-1.69	4.65	0.264	-0.26	3.04	0.275	-0.31	3.30
5.50	0.401	-1.73	4.42	0.263	-0.28	3.00	0.265	-0.21	3.22
5.60	0.402	-1.74	4.18	0.264	-0.30	2.96	0.256	-0.13	3.14
5.70	0.402	-1.74	3.94	0.265	-0.32	2.90	0.246	-0.05	3.05
5.80	0.398	-1.69	3.70	0.265	-0.35	2.84	0.236	0.05	2.98
5.90	0.394	-1.63	3.49	0.265	-0.37	2.77	0.227	0.13	2.92
6.00	0.385	-1.51	3.26	0.266	-0.39	2.69	0.218	0.22	2.86

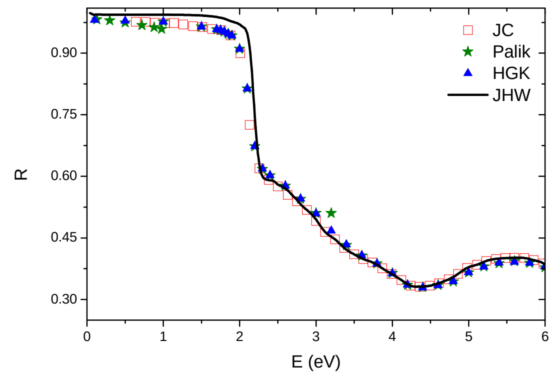

Figure 1. Reflectance for Cu. Below ~ 2 eV, the reflectance of JHW (J. H. Weaver) is higher than for the films of JC (Ref. 9), HGK (Ref. 7,8), and Palik (Ref. 5). Palik extracted the data from two sources and a discontinuity in R is apparent, as is a typo at ~ 3

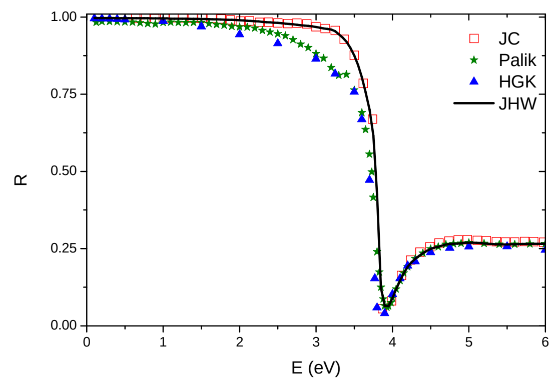

Figure 2. Reflectance for Ag shows excellent agreement in R between JC and JHW

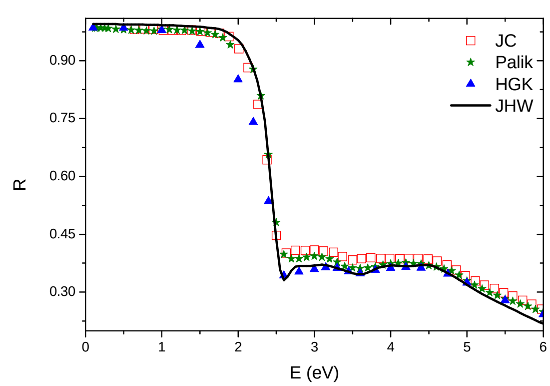

Figure 3. Reflectance for Au. The solid line, JHW, reproduces the reflectance results from Ref. 2

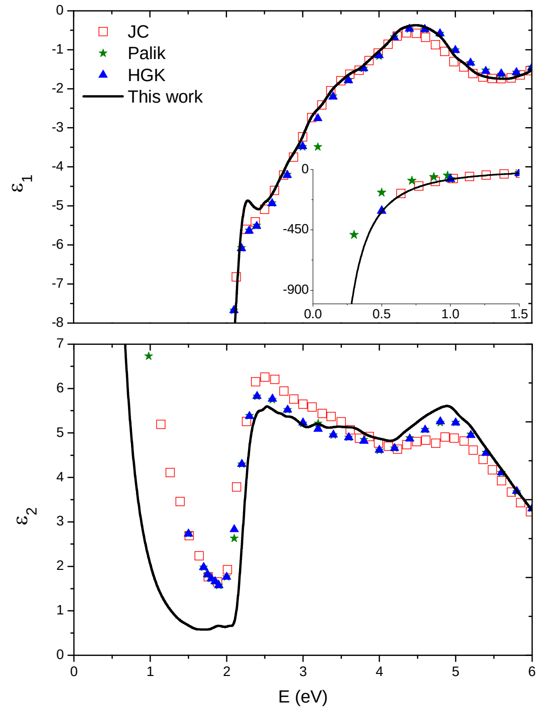

Figure 4. Dielectric constants for Cu

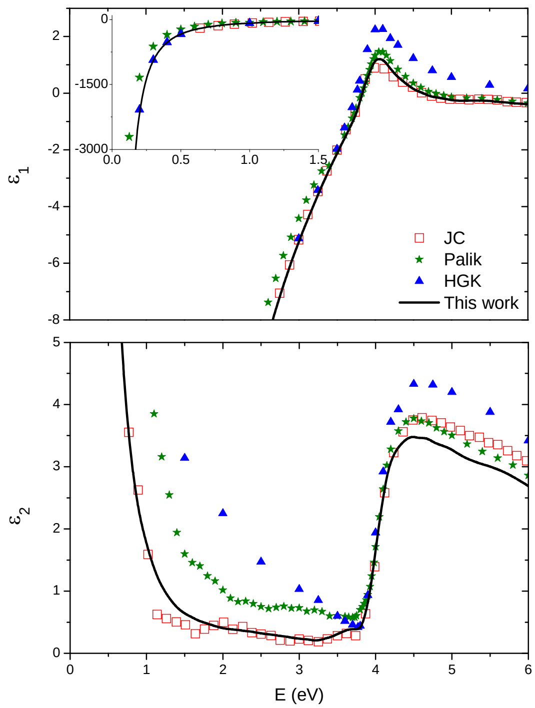

Figure 5. Dielectric constants for Ag

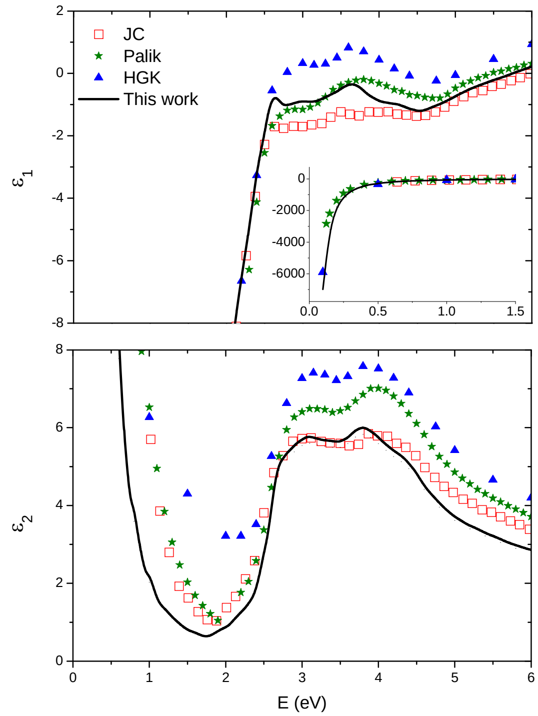

Figure 6. Dielectric constant for Au