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Photoelectric Work Functions of Transition, Rare-Earth, and Noble Metals

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Photoelectric work functions of polycrystalline films of Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Y, Zr, Nb, Mo, Pd, Ag, La, Ce, Nd, Sm, Eu, Gd, Hf, Pt, and Au are reported.

There exists a wealth of experimental data on work functions of transition and noble metals.¹⁻²⁰ However, much scatter is observed in the published data¹ which is due, in part, to the sensitivity of work functions to surface conditions. We present photoelectric work functions for a number of metals (see Table I) which were prepared in ultrahigh vacuum, using electron-beam-gun evaporation techniques.²¹ Such experimental data should be useful in studies of various surface effects, including theoretical studies²² of the complicated phenomena (exchange and correlation effects, etc.) involved in the surface potential barrier. Several empirical correlations have been made relating the work functions of metals to electronegativities, atomic volume, etc.^{1,23,24} The work functions listed in Table I in general show such correlations.

Polycrystalline films of ~1000 to 2000 Å thickness were evaporated at rates of ~2-5 Å/sec onto Cr-plated optically smooth quartz substrates. Pressures in the vacuum chamber typically rose to ~10⁻⁹-10⁻⁸ Torr during evaporation, and then rapidly fell to the 10⁻¹⁰-Torr range within a few minutes after completion of the evaporation. Films of several transition metals (Ni, Co, Cr, Gd) were subsequently studied by electron diffraction and were found to consist of randomly oriented crystallites with dimensions ~100-200 Å.

The photoelectric work functions were determined at room temperature by measuring the quantum yield $Y(\omega)$ versus photon energy $\hbar\omega$ just above threshold, and using a Fowler plot,²⁵ i. e.,

$$[Y(\omega)]^{1/2} \propto \hbar\omega - \phi,$$

where ϕ is the work function. The tolerances

given in Table I include the reproducibility of several specimens as well as the uncertainty involved in the Fowler plot.

For comparison with our data, other photoelectric and thermionic work-function measurements¹⁻²⁰ are given in Table I. These references were selected on the basis that they are probably the most reliable photoelectric and thermionic

TABLE I. Photoelectric work functions.

Element	ϕ (eV)	ϕ^a (Photoelectric)	ϕ^a (Thermionic)
Sc	3.5 ± 0.15
Ti	4.33 ± 0.1	4.45 ²	3.6-4.3 ¹⁴
V	4.3 ± 0.1	...	4.12 ¹⁵
Cr	4.5 ± 0.15	4.68 ³	3.9 ¹⁴
Mn	4.1 ± 0.2	...	3.83 ¹⁵
Fe	4.5 ± 0.15	4.8 ⁴	4.47 ¹⁴
Co	5.0 ± 0.1	4.5 ⁵	4.41 ¹⁶
Ni	5.15 ± 0.1	5.0 ⁶	4.50 ¹
Cu	4.65 ± 0.05	4.5 ⁷	4.42 ¹⁴
Y	3.1 ± 0.15
Zr	4.05 ± 0.1	4.33 ²	3.9 ¹
Nb	4.3 ± 0.15	4.33 ⁸	4.19 ¹⁷
Mo	4.6 ± 0.15	4.3 ⁹	4.0-4.3 ¹⁷
Pd	5.55 ± 0.1	5.5 ¹⁰	4.9 ¹⁸
Ag	4.0 ± 0.15	4.0 ¹¹	4.3 ¹
La	3.5 ± 0.2	...	3.3 ¹⁹
Ce	2.9 ± 0.2	...	2.7 ¹⁹
Nd	3.2 ± 0.25	...	3.3 ¹⁹
Sm	2.7 ± 0.3	...	3.2 ¹⁹
Eu	2.5 ± 0.3
Gd	3.1 ± 0.15	3.1 ¹²	...
Hf	3.9 ± 0.1	...	3.5 ¹⁸
Pt	5.65 ± 0.1	5.2 ¹³	5.6-5.8 ¹⁴
Au	5.1 ± 0.1	4.9 ¹¹	5.22 ²⁰

^aSuperscripts denote source references. Data quoted for Ref. 1 represent recommended values.

work functions which we located in a literature search (an emphasis has been placed on recent work). In many instances, our values are somewhat higher than previously reported values, especially those reported by Fomenko.¹ In general, the thermionic work functions in Table I are smaller than our photoelectric values. For many metals, this is believed to be due to surface contamination. We have observed changes in work functions of the order of a few tenths of an eV for

very slight surface contamination (O_2 , water vapor, etc.). Usually, the work function becomes smaller subsequent to surface contamination, especially for materials with work functions greater than ~ 4 eV. Partial crystalline orientation of film specimens can account for observed differences in some cases, since anisotropies of ~ 0.5 eV exist for different crystal faces.^{1,24}

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