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Photoemission and Optical Investigation of the Electronic Structure of Ruthenium†

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Photoemission and optical studies on vapor-deposited films and bulk samples of ruthenium are reported for the spectral range below 12.0 eV. The photoemission data locate structure in the d-like states at 0.5, 1.3, and 3.6 eV below the Fermi energy, and they show no structure due to states above the vacuum level. The data were found to be consistent with the nondirect model, with the possible exception of a small decrease in the amplitude of the structure at $E-E_F=-0.5$ eV for $h\nu>10$ eV. A combined analysis of the optical and photoemission data locates a strong peak in the d-like density of states about 1.5 eV above the Fermi energy. The studies are discussed with respect to band calculations, data for related metals, and the absence of an isotopic-mass dependence of the superconducting transition temperature. Photoemission data from a material tentatively identified as ruthenium oxide are presented.

I. INTRODUCTION

The transition metals, which contain partially filled d states, exhibit many diverse physical properties which are not found in simple metals. These properties are not easily predicted from a knowledge of the metal's atomic electron configuration as exemplified by ruthenium ($4d^7 5s^1$) which is hexagonal and nonmagnetic and by iron ($3d^7 4s^1$) which is bcc and ferromagnetic. In contrast with the $M^{-1/2}$ isotopic-mass dependence of the superconducting transition temperature found in simple metals, the transition metals exhibit many deviations.[1] The largest deviation is found in Ru which appears to have no such isotopic-mass dependence. The deviation in Ru has been treated theoretically with models that require special properties for the electronic density of states.[1,2] Few experimental studies have been reported on Ru.

We report here a study of the electronic structure of Ru using photoemission and optical data in the spectral region below 12 eV. Since, with one possible exception, the photoemission data had nondirect character over a wide range of photon energies, the photoemission data and optical studies were combined to define an optical density of initial and final states of electrons per unit energy. The optical measurements were done on vapor-deposited films of Ru. The photoemission measurements were taken from vapor-deposited films and a heat-treated bulk sample. The bulk sample provided a check for possible grain size or stress effects.

II. EXPERIMENTAL PROCEDURE

Photoemission measurements were made on vapor-deposited films of Ru under high-vacuum conditions. The films were deposited from an electron beam gun located about 0.5 m below the photocathode. The photocathode was hinged so that it could be moved into the photocollector after the vacuum deposition. Films were prepared from ingots obtained from two suppliers.[3] The photoemission data from both of these samples compared well for all films deposited below 5×10^{-8} Torr. The best pressure obtained during the deposition was $\sim1\times10^{-8}$ Torr with a base pressure of $\sim7\times10^{-10}$ Torr achieved several min after completion of the deposition.

Photoemission measurements were also performed on a sheet of bulk Ru processed by heat treating in the vacuum. A small 2×2-cm sheet was polished and degreased before spot welding onto tantalum supports. The sample was heated from behind by electron bombardment. The sheet of Ru could be heated to 1700 °C as measured by an optical pyrometer. Although the polished sheet was

smooth initially, and quite featureless well-defined grain boundaries were apparent after several heat treatments. The average grain size was a few tenths of a mm.

The details of the photoelectron energy distribution curve (EDC) measurement and the quantum yield measurement have been reported.[4-6] The EDC's were measured by the method of retarding potentials, using a gold-coated cylindrical collector. The quantum yield was measured relative to sodium salicylate and calibrated absolutely at 10.2 eV using a NO photocell.

The near-normal-incidence reflectance from films of Ru vapor deposited onto a microscope slide substrate was measured. The films were prepared in the same manner described above and under similar vacuum conditions.

III. RESULTS

A. Optical Studies

The near-normal-incidence reflectance of Ru is presented in Fig. 1. The reflectance data were measured between 0.5 and 11.8 eV under high-vacuum conditions. The data were extended to 14.0 eV by using the shape of the reflectance obtained from a polished sample of Ru which had been exposed to air. The latter data reduced the range of the high-photon-energy extrapolation used in the data analysis. The extrapolation to zero energy was done with the Hagen-Rubens formula. A shallow relative minimum occurs at 1.6 eV and relative maximum at 2.0 eV. The reflectance falls with increasing energy until a second relative minimum occurs at 11.6 eV.

The optical constants were calculated from the normal-incidence reflectance by a Kramers-Krönig (KK) analysis which used a power-law extrapolation for $h\nu \geq 14$ eV. A complete discussion

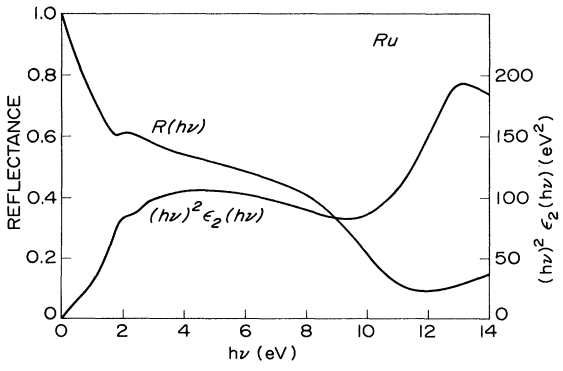

FIG. 1. Spectral dependence of the normal-incidence reflectance and the imaginary part of the dielectric constant multiplied by the photon energy squared of Ru.

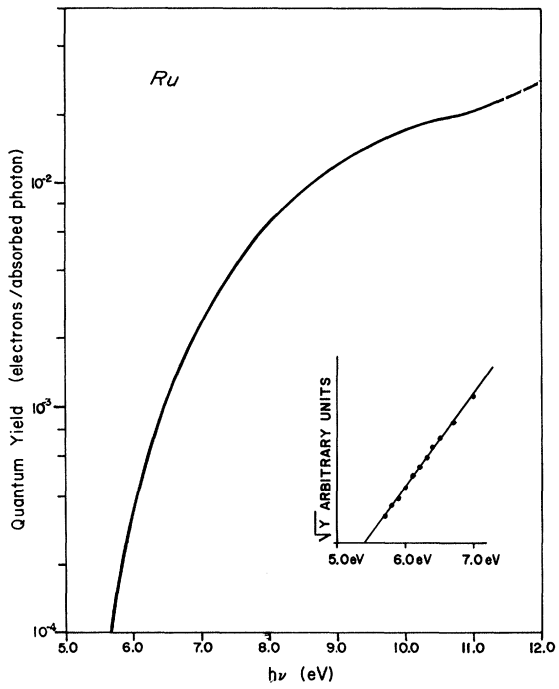

FIG. 2. Spectral dependence of the absolute quantum yield of vapor-deposited Ru films. The insert is used to determine the work function of 5.4 eV.

of the optical study has been reported.[5,7] The imaginary part of the dielectric constant multiplied by the photon energy squared $(h\nu)^2\epsilon_2$ is proportional to the quantum transition probability over all final states.[8] A shoulder is found in the latter function at 2.0 eV followed by a broad structure centered at ~6.0 eV. The optical constants in the spectral region near and beyond 12.0 eV can be distorted by the high-photon-energy extrapolation. It is noted here that the energy-loss function $\mathrm{Im}(1/\epsilon)$ has a peak at 10.2 eV with a half-width of approximately 4.0 eV.

B. Photoemission Studies

The absolute quantum yield for vapor-deposited films of Ru is displayed in Fig. 2. The work function ϕ for polycrystalline Ru is 5.4 eV and is determined by the square root of the yield plot shown in Fig. 2.

A representative set of the EDC's from vapor-deposited films of Ru are shown in Fig. 3. The curves are plotted as a function of $E - h\nu$, the initial-state energy, where the zero of the energy is the Fermi energy. The EDC's have three peaks labeled 1–3 that result from initial-states structure. Peaks 1 and 2 are located at -0.5 and -1.3 eV, respectively. Peak 3 at approximately $E - h\nu \simeq 3.6$ eV appears to have $E - h\nu$ dependence, but is

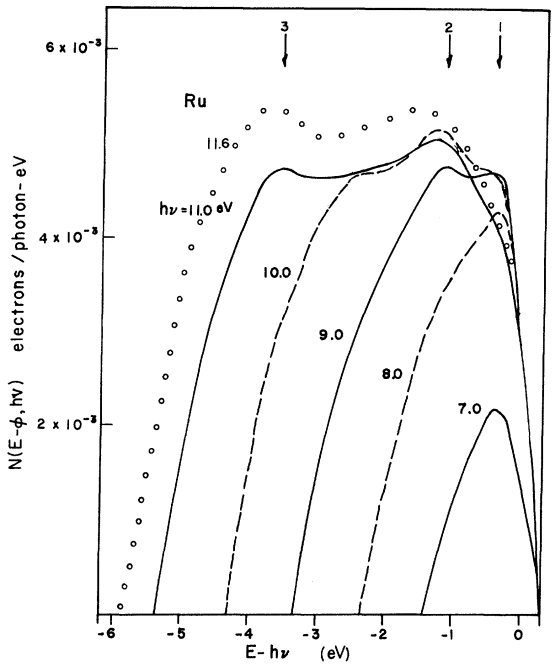

FIG. 3. Normalized energy distributions of photoemitted electrons from Ru, plotted as a function of initial energies $E-h\nu$.

produced by states which are too far below the Fermi energy to be thoroughly studied within the available spectral range. In addition, the functional dependence of peak 3 is difficult to determine at the high photon energies because of the increasingly large fraction of scattered electrons in the EDC's. No structure was found in the EDC's with final-state dependence.

A bulk sheet of Ru was studied by photoemission techniques. The sheet was heat-treated three times in vacuum. The EDC's obtained after the initial heating were not characteristic of the data obtained from clean Ru but are of sufficient interest to be discussed in the Appendix. The data from the bulk sample became more like the vapor-deposited film data, after the bulk sample was subjected to more thorough heat treatments. The final heating was for several days at $\simeq 1200\,^{\circ}$C followed by a few second flash at $\sim 1700\,^{\circ}$C. The similarities between the bulk and film studies are shown in Fig. 4.

Because the work function of the bulk sample was 1.1 eV lower than that observed for the film samples the curves compared in Fig. 4 differ by 1 eV. Peaks 1–3 at $E-h\nu = -0.5$, -1.3, and -3.6 eV are seen in both sets of data. Between peaks 2 and 3 in Fig. 4 there is another peak which has final-state energy dependence. Since the latter peak was found to have the same properties as the most prominent peak in the EDC's obtained after the first heating (see the Appendix), it is attributed to residual amounts of ruthenium oxide left on the surface of the bulk sample.

In addition film and bulk samples were cesiated and studied. Peaks 1 and 2 were observed in the EDC's. Peak 3, however, could not be studied because the EDC's show an extremely strong peak with initial-state character which is not due to simple scattering effects nor to the intrinsic properties of Ru.

An additional peak was found in the EDC's obtained from samples that were allowed to age, that had been exposed to higher pressures, or that had been formed at pressures greater than 5×10^{-8} Torr. The peak is shown in Fig. 5, where a clean sample was briefly exposed to a pressure of $\sim 1\times10^{-7}$ Torr. The additional peak has initial-state character and is located at $E-h\nu = -2.8$ eV. The work function of this sample decreased by approximately 0.2 eV which is typical of the data containing the additional peak. The EDC's had increased scattering as indicated by the attenuation of high-energy electrons and an increase of low-energy electrons. This structure has many of the same characteristics of a similar peak observed from aged films of dysprosium.[9] Because of these similarities, much of the

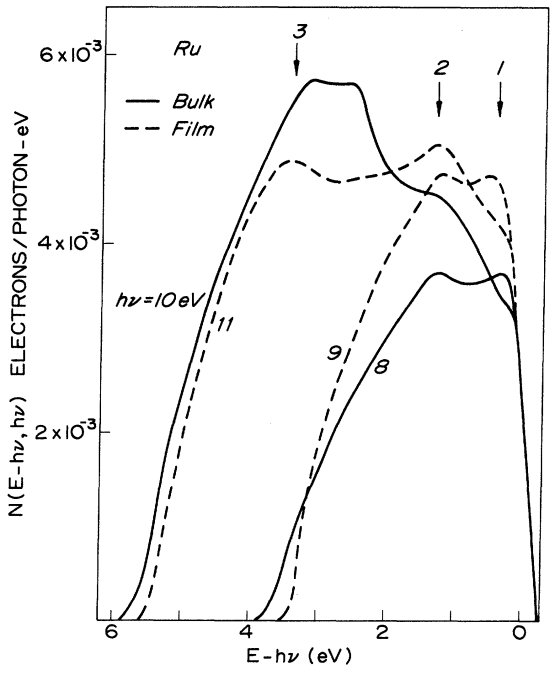

FIG. 4. Comparison of energy distribution curves from bulk samples (—) and vapor-deposited film samples (– –) of Ru plotted as a function of initial-state energy $E-h\nu$.

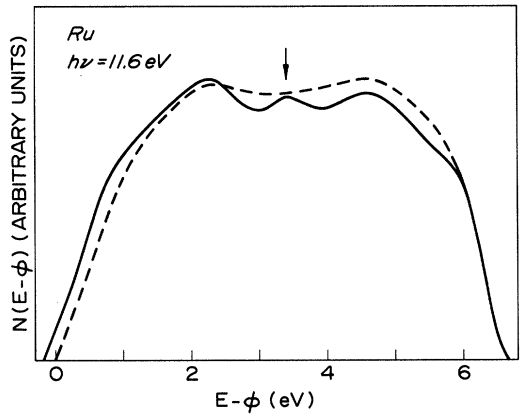

FIG. 5. Energy distribution curves from Ru before (– –) and after exposure to 1×10^{-7} Torr (—) plotted as a function of kinetic energy $E-\phi$.

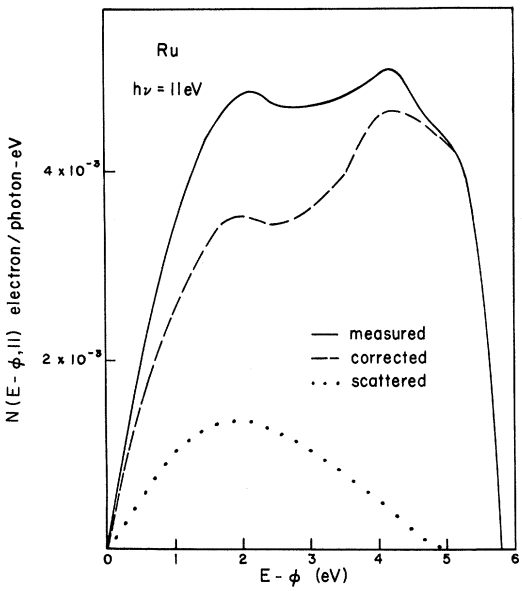

FIG. 6. Measured, computed once-scattered, and corrected for once-scattered energy distribution curves of photoemitted electrons from Ru at $h\nu=11.0$ eV.

discussion given there concerning the possibility and character of the contamination would apply here.[10]

C. Desnity-of-States Analysis

An optical density of states (ODS)[11] was determined for Ru since the photoemission data are consistent with the nondirect model. The details of the analysis procedure used to obtain the ODS have been given.[4,5] The model was used with the approximation that the photoelectron escape length is small with respect to the optical absorption depth. The relative values of the latter parameters are confirmed by the observed small magnitude of the yield. Before determining the ODS below the Fermi energy, the EDC's were corrected for escaping once-scattered electrons by use of the scattering model of Berglund and Spicer.[8] An example of the scattering contribution at $h\nu=11.0$ eV is shown in Fig. 6. The ODS above the Fermi energy was obtained from the nondirect model by a numerical analysis technique which used the ODS below the Fermi energy and the imaginary part of the dielectric constant ϵ_2.[4,5] The latter technique will generate an ODS which can be used to calculate ϵ_2 with arbitrary accuracy. The ODS found is given in Fig. 7 by the solid curve. The states for $|E|\gtrsim 4.5$ eV cannot be studied with confidence because of the spectral limits imposed by the LiF window used on the vacuum chamber. These less reliable regions are indicated by dots. The fine structure seen on the ODS for $E>4.0$ eV is a result of the details of the numerical analysis used to find the ODS for $E>E_F$. The lack of structure, however, for $E>\phi$

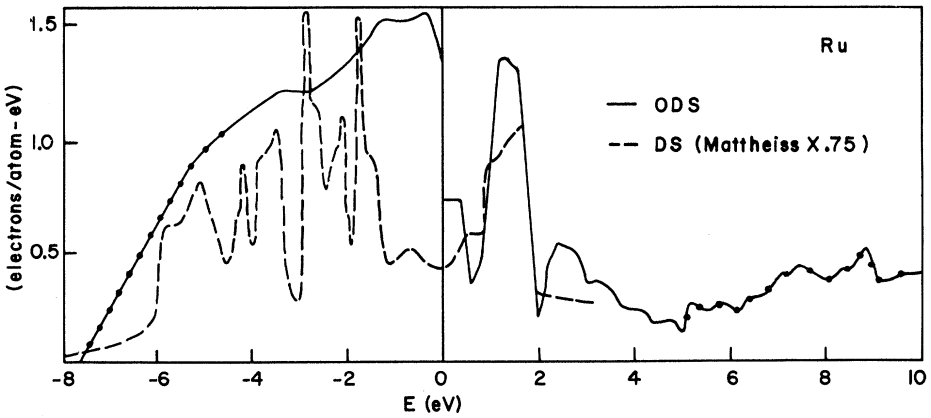

FIG. 7. Comparison of the Ru ODS with the DS estimated from Mattheiss's Re band-structure calculation (Ref. 12).

in the ODS agrees with the observation of no final structure in the EDC's. The results obtained from the ODS analysis reproduced the shapes of all the measured EDC's within a few percent. The relative magnitudes of the EDC's were reproduced for $\phi < h\nu \lesssim 10.0$ eV; however, for $h\nu \gtrsim 10.0$ eV the magnitudes of the reproduced EDC's were too small. The latter disagreement results from the strong increase in $(h\nu)^2\epsilon_2$ for $h\nu \gtrsim 10.0$ eV without a compensating increase in the quantum yield (see Figs. 1 and 2).

IV. DISCUSSION

The ODS of Ru is compared in Fig. 7 to a density of states (DS) obtained from band calculations. The comparison of the ODS of hcp Ru was done by shifting the Fermi energy of the DS of hcp rhenium[12] to produce one additional filled state and by contracting the energy scale by a factor of 0.75. The energy scale factor was estimated from the energy eigenvalue differences between various symmetry points in the Brillouin zone of Re compared to the same energy eigenvalue differences for Ru.[13]

The agreement seen in Fig. 7 between the observed ODS and the calculated DS above the Fermi energy is better than expected. Below the Fermi energy there is little agreement. The only possible correlation is in the number of peaks: two near E_F followed by a broad peak at lower energies. The difference in widths of the structures seen in Fig. 7 is principally a result of the lifetime broadening of the structures in the EDC's. A major discrepancy exists between the ODS and DS at and just below E_F. The calculated DS and the electronic heat-capacity data[1] indicate a small density of states at E_F while the ODS is comparatively large at E_F. The general d-like bandwidths of 2 eV for the empty states and 6 eV for the filled states are in agreement in the ODS and DS.

The photoemission EDC's of hcp Ru are similar to the EDC's of hcp cobalt.[14] The derived ODS's are similar also. The EDC's from both Ru and Co contain two peaks in the initial states near the Fermi energy and a high DS at the Fermi energy. In addition, a third weak peak is indicated a few eV below the Fermi energy in the photoemission data from both studies. The latter comparison is not dependent on the optical transition selection rule. The similarity between the data from the two metals is not expected from the rigid-band model since Ru has one less electron than Co.

The population of high-energy electrons in the EDC's suddenly deteriorates for photon energies between 10 and 11 eV as seen in Fig. 3. This loss of high-energy electrons may be associated with discrete energy losses indicated by the observed maximum in the energy-loss function $\mathrm{Im}(1/\epsilon)$, at

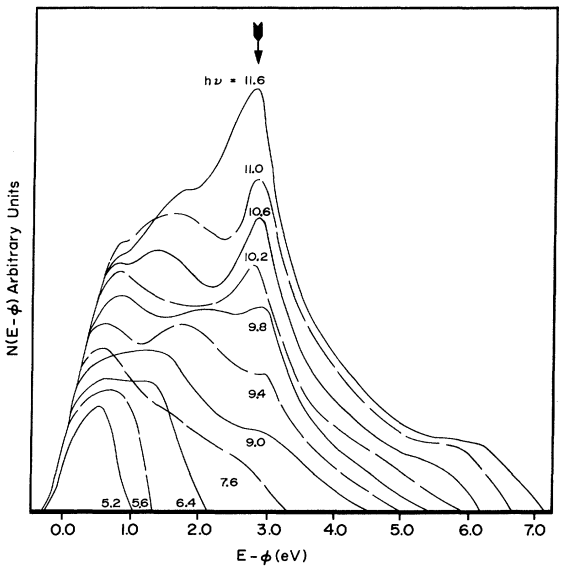

FIG. 8. Energy distribution curves from bulk sample of Ru after one vacuum heat treatment at approximately 1000 °C. The curves are arbitrarily normalized and plotted as a function of kinetic energy.

10.2 eV. Stronger but otherwise similar effects on the EDC's of zinc have been associated with large discrete energy losses.[15] Alternately the sudden attenuation of the high-energy electrons could indicate direct transition character for peak 1. Recent direct transition model calculations for the energy distributions from copper[16] and palladium[17] indicate that the principal characteristics of the distributions obtained from the direct and nondirect models cannot be unambiguously distinguished by the experimental EDC's. Similar effects may be contained in the photoemission data from Ru.

An anomalous d-band peak in the density of states near the Fermi energy of Ru has been proposed to explain the lack of an isotopic mass effect in Ru's superconducting transition temperature.[2] Although the optical studies of this work did not extend below 0.5 eV, the photoemission data does probe the DS in the vicinity of the Fermi energy. Within the resolution of the photoemission experiment, no large amplitude narrow structure was observed near the Fermi energy. In agreement with this finding, a recent theoretical treatment of the isotopic-mass effect[1] explains the absence of the isotopic-mass dependence without any anomalous conditions being imposed on the DS.

APPENDIX: RUTHENIUM OXIDE STUDIES

During the sequence of heat cleaning a bulk sheet of Ru at successively higher temperatures, a set of photoemission EDC's was obtained which are characteristic of a "clean" sample, but not of Ru. The EDC's are shown in Fig. 8. The EDC's, as is

typical of clean samples, have well-defined structures and do not contain appreciable numbers of low-kinetic-energy electrons. The sample was obtained by heating a Ru sheet at 1000 °C for 24 h at a pressure of $5-10\times10^{-8}$ Torr.

The data have strong direct transition properties and have strong final-state structure. One very prominent final-state peak (arrow in Fig. 5) is observed with fixed kinetic energy at about $E-\phi=2.9$ eV. Two final-state structures are observed at $E-\phi=1.1$ eV and $E-\phi=0.9$ eV in the spectral ranges $6\lesssim h\nu\lesssim 7.0$ eV and $10\lesssim h\nu\lesssim 11.8$ eV, respectively. Four structures are noted in the EDC's whose positions are nearly proportional to the photon energy, but the proportionality constants β_i, are not all unity. As the photon energy is varied, the appearance and disappearance of these four structures is abrupt. Two of the latter structures with $\beta\approx1$ are observed near the Einstein limit of the EDC's in the spectral ranges $\phi<h\nu<7.0$ eV and $10.5<h\nu<11.8$ eV. The two remaining major structures have β's less than unity and their positions E_A and E_B are given within a few tenths eV by

$$E_A-\phi=0.67[h\nu-6.7]\ \text{eV for } 7.5<h\nu<10.0\ \text{eV},$$

$$E_B-\phi=0.61[h\nu-8.3]\ \text{eV for } 9.0<h\nu<11.8\ \text{eV}.$$

It is suggested that these EDC's are from RuO_2 since the dioxide of Ru is known to be formed at temperatures above 800 °C. Between 800 and 1150 °C, there is simultaneous formation of another oxide which has a much larger vapor pressure.[18] The latter form is probably the monoxide, and since the monoxide is the only oxide present at temperatures above 1150 °C, the dioxide is probably what was studied. Subsequent heat treatment produced EDC's similar to those obtained from Ru films indicating that most of the oxide was removed.

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