Low-Energy Optical Absorption in ReO3

J. H. Weaver
Iowa State University

David W. Lynch
Iowa State University, dlynch@iastate.edu

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Abstract
The absorptivity of polycrystalline samples of ReO3 has been measured in the range 0.11 to 2.8 eV using a calorimetric technique. New structures have been found in the absorptivity, appearing at about 0.4 and 1.0 eV. The data have been Kramers-Kronig analyzed to obtain the optical constants. Band-calculation results of Mattheiss are presented and a tentative identification of the origin of the new structures is made. A comparison of the present data with those of Feinleib, Scouler, and Ferretti is made.

Keywords
calorimetric, low-energy transitions, Ames Laboratory

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Comments
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J. H. Weaver and D. W. Lynch

Ames Laboratory, U. S. Atomic Energy Commission and Department of Physics
Iowa State University, Ames, Iowa 50010

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The absorptivity of polycrystalline samples of ReO₃ has been measured in the range 0.11 to 2.8 eV using a calorimetric technique. New structures have been found in the absorptivity, appearing at about 0.4 and 1.0 eV. The data have been Kramers-Kronig analyzed to obtain the optical constants. Band-calculation results of Mattheiss are presented and a tentative identification of the origin of the new structures is made. A comparison of the present data with those of Feinleib, Scouler, and Ferretti is made.

INTRODUCTION

A variety of studies have recently contributed to an understanding of the transition-metal oxide ReO₃. It has been shown that ReO₃ is a good electrical conductor, is nonmagnetic, and possesses a cubic crystal structure. Information concerning the band structure of ReO₃ at the Fermi level has been provided by the de Haas–van Alphen (dHvA) measurements of Marcus,¹ the magnetothermal...
measurements of Graebner and Greiner, and the optical measurements of Feinleib, Scouler, and Ferretti (FSF). A detailed calculation of the band structure and Fermi surface has been conducted by Mattheiss. Following these calculations, Phillips and Shanks performed additional dHvA measurements and observed three new orbits, in agreement with those predicted.

In the band scheme of Mattheiss, degenerate bands cross the Fermi level and are split by spin-orbit interaction. The resulting nearly parallel bands should lead to a large joint density of states for interband transitions which would produce structure in the infrared optical spectrum, selection rules permitting. Since the measured reflectivity data of FSF were rather "noisy" in the infrared, we have investigated the region from 0.11 to 2.8 eV using a technique which is particularly suited for low-energy measurements. The results presented here do show that such infrared transitions exist and lend further credence to the band calculations of Mattheiss.

RESULTS AND DISCUSSION

Calorimetry provides an excellent technique for measuring the absorptivity \( A = 1 - R \) of metals, particularly in the spectral region where the absorptivity is small. The advantage lies in the measurement of a small quantity \( A \) instead of the relatively large quantity \( R \), with the same degree of relative accuracy. Generally, \( A \) is measured at near-normal incidence and any effects due to transparent gases which have condensed on the surface are small.

Absorptivity measurements at 4.2 K were carried out at near-normal incidence on samples of polycrystalline ReO\(_3\). The technique employed and equipment used have been described elsewhere. The samples were grown by an iodine-vapor-transport technique and typically had surface dimensions of \( 6 \times 12 \) mm. The data presented here were obtained using an as-grown sample with a very smooth surface. Measurements were also performed using crystals having rough surfaces. The results were qualitatively the same, i.e., all exhibited the same infrared structure, while, of course, the magnitude of \( A \) was affected by the surface roughness. Attempts were made to polish a typical rough sample, but it was too brittle and irregular to permit a fine polishing. The partially polished sample was studied nonetheless and the results agreed qualitatively with those reported.

The measured absorptivity of ReO\(_3\) is shown in Fig. 1. The relative accuracy in the measured quantity is estimated to be 1% (e.g., at 0.4 eV, \( A = 0.1875 \pm 0.002 \)). Two shoulders are clearly evident in the spectrum of Fig. 1 with peaks at about 0.4 and 1.0 eV, and are presented for the first time. The sharp reflectivity minimum reported by FSF at 2.3 eV is also shown. In addition to the low-energy shoulders in \( A \), a sharp narrow spike (height of 1%, half-width of 0.01 eV) followed by a slight dip in \( A \) was observed. This appears in the region from 0.13 to 0.17 eV, too high in energy to be identified as belonging to the phonon spectrum. (Raman studies have revealed structure in Na\(_2\)WO\(_4\) and Rb\(_2\)WO\(_4\) in the region from 0.025 to 0.050 eV—considerably further in the infrared than this peak.) Since our crystals were not electropolished or etched, it seems probable that this structure can be attributed to a surface film of some sort. Accordingly, no effort was made to assign physical meaning to it. For the Kramers-Kronig analysis, the peak was ignored, lest it appear in the dielectric function as a sharp spike.

The absorptivity data have been analyzed using a standard Kramers-Kronig (KK) technique which calls for data over a large energy range. The reflectivity data of FSF were used from 2.8 to 22 eV; a shift was not needed to match the respective sets of data. For energies above 22 eV, a smooth extrapolation was used. A Drude-like behavior was assumed in the infrared beyond 0.11 eV.
The optical conductivity $\sigma$ is presented in Fig. 2. Only our results are shown and no attempt is made to compare with those of FSF because the presence of low-energy structure significantly alters both the shape and magnitude of $\sigma$. It should be noted that while the new infrared features affect the optical constants computed by FSF in the infrared, we have found that there is no appreciable change in the range $E \geq 3.5$ eV. Thus a compilation of the dielectric constants $\epsilon_1$, $\epsilon_2$ (or $n$, $k$) would include our values for $E \geq 3.5$ eV and the data of FSF for the remainder of the spectrum. Our computed $\epsilon_1$, $\epsilon_2$ are shown in Fig. 3.

The band-structure calculations of Mattheiss for ReO$_3$ are shown in Fig. 4(a). Augmented-plane-wave (APW) calculations were performed using an ad hoc potential derived from neutral-atom charge densities, including a correction to the usual muffin-tin potential outside the APW spheres. The results of the APW calculations at the symmetry points $\Gamma$, $X$, $M$, and $R$ were used to determine the parameters for a linear-combination-of-atomic-orbitals (LCAO) tight-binding approach to find $E$($k$) for all other points shown. The details of the band calculations are given in Ref. 6. The bands shown in Fig. 4(a) include those arising from the rhenium 5$d$ orbitals and $s$-$p$ or nearly-free-electron-type bands. No attempt has been made to reproduce those bands which arise from the oxygen 2$p$ states as these bands appear below the Fermi level by energies in excess of our maximum photon energy.

The bands shown in Fig. 4(a) were calculated assuming no spin-orbit interaction of the rhenium 5$d$ states. When the spin-orbit interaction is introduced, the degeneracy of the bands along $TX$, $TM$, $TR$, $RX$, and $RM$ is partially lifted. As is

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**FIG. 3.** Dielectric constants $\epsilon_1$ (dashed) and $\epsilon_2$ (solid) vs. energy. A comparison with the data of FSF shows good agreement for $E \geq 3.5$ eV. The inset displays $\epsilon_2$ in the neighborhood of the 0.4-eV structure. While $\epsilon_1$ has a distinct kink at about 0.5 eV, the spectrum of $\epsilon_2$ is smoother and the structure is more clearly seen in the conductivity.

**FIG. 4.** (a) Energy bands of ReO$_3$ as calculated by Mattheiss (Ref. 4) without spin-orbit effects. It is seen that along the direction $\Sigma$, $\Sigma_1$, and $\Sigma_3$ are roughly parallel to $\Sigma_4$. (b) Energy bands of ReO$_3$ showing how the bands have been split by spin-orbit effects. It is seen that the structure of Fig. 2 can be attributed to transitions along $\Delta$, $\Sigma$, $\Lambda$ and nearby regions of $k$ space. Spin-orbit effects have removed the degeneracy of $\Lambda_4$ and $\Lambda_6$, $\Lambda_6$, but the separation is too small to show here (see Ref. 4).
seen in Fig. 4(a), parallel bands cross the Fermi level along the directions $\Delta$, $\Sigma$, and $\Lambda$ and probably extend throughout a considerable volume of $k$ space near these directions. As a result, a large joint density of states is expected and corresponding structure in the interband dielectric function and conductivity is likely.

In Fig. 2 the optical conductivity obtained from our KK analysis is plotted as a function of energy. Two structures are clearly visible against the free-electron or Drude background. These occur at roughly 0.4 and 1.0 eV. It can be inferred that the structure at 0.4 eV probably results from transitions along $\Delta$, $\Sigma$, and $\Lambda$ and nearby regions of $k$ space, corresponding to transitions from the lower of the spin-orbit bands to the upper band. The transitions $\Delta_4 - \Delta_7$, $\Sigma_5 - \Sigma_4$, and $\Lambda_4$, $\Lambda_5$, $\Lambda_6 - \Lambda_8$ are all allowed by selection rules. Since the respective bands are separated by small, but unequal, amounts, the observed structure is expected to be relatively broad (it is roughly 0.3 eV wide). Further, the structure at 1.0 eV can probably be identified as resulting from the transitions $\Sigma_4 - \Sigma_5$ corresponding to the transitions $\Sigma_4 - \Sigma_4$ and $\Sigma_4 - \Sigma_1$ in the single-group notation of Fig. 4(a). It is seen that $\Sigma_4$ is only roughly parallel to $\Sigma_3$. This would reduce the joint density of states and account for the relatively small size of the structure.

CONCLUSION

It has been seen from the data presented here that low-energy transitions of the sort predicted by Mattheiss do exist in ReO$_3$. While our identification of the origin of the transitions must of necessity be rather cautious (energy bands are known only along the symmetry lines), it is clear that qualitatively at least the calculated bands are in agreement with our experimental data. A further calculation of the optical interband transition matrix elements as done by Kasowski in the case of zinc would provide more quantitative comparisons of experimental and theoretical results.

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8. Our crystals were provided by H. R. Shanks who performed an analysis of the ReO$_3$ and found a total of 200 ppm impurities with the major impurities being B (40 ppm), Na (30 ppm), Cl (50 ppm), and Y (40 ppm); no iodine was found.
11. Preliminary results from studies on Na$_2$WO$_4$ and K$_2$WO$_4$ show no such structure for energies above 0.1 eV. Similarly, earlier studies with the same apparatus have never revealed such spikes; we do not attribute the structure to experimental apparatus.
12. Normalized reflectivity data in the vacuum ultraviolet from 22–36 eV indicated that $R$ drops smoothly from 9.6% (normalized to FSF) at 21.8 eV to 6.7% at 30 eV, to 3.9% at 36 eV. To extend the range further, an extrapolation was introduced which matched the experimental $E$ vs $R$ slope at 36 eV and forced $R$ to drop smoothly to zero at 1000 eV.
13. The magnitude of the spin–orbit splitting was estimated in Ref. 6 to be 0.6 eV for $E(\Gamma_6^*) - E(\Gamma_7)$.