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Study of the Electronic Structure of ReO₃ and its Pressure Dependence by the Korringa-Kohn-Rostoker Method

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Energy bands of the simple cubic metallic compound rhenium trioxide have been calculated by using the Korringa-Kohn-Rostoker method. The crystal potential has been constructed in the muffin-tin approximation from overlapping atomic charge densities and full Slater exchange. As a result of the muffin-tin approximation, the rhenium d band comes out too narrow, but the band ordering and the Fermi-surface geometry agree well with the more elaborate calculations. The calculation has been done for both an equilibrium lattice and a compressed lattice, and the changes in Fermi-surface geometry have been investigated. It is found that the logarithmic derivatives of some de Haas-van Alphen frequencies with respect to pressure depart markedly from the free-electron scaling predictions, in agreement with the experimental results.

INTRODUCTION

Rhenium trioxide was found to be an excellent metal by Ferretti *et al.*,[1] having an electrical conductivity of $2.5 \times 10^6 \ \Omega^{-1} \ \mathrm{cm}^{-1}$ at 77 K. At room temperature the conductivity is of the order of $10^5 \ \Omega^{-1} \ \mathrm{cm}^{-1}$, which is within an order of magnitude of copper. Narath and Barham[2] deduced from NMR studies that the conduction-electron states of ReO₃ at the Fermi level are derived mainly from atomic d states.

Mattheiss[3,4] carried out a series of band calculations for ReO₃. He found that the augmented-plane-wave (APW) method converges very slowly, so that it requires 250 APW basis functions. To get a band on a fine mesh over the momentum space he used the Slater-Koster interpolation method between the APW results at high-symmetry points. The resulting conduction band is in-

deed the d band of rhenium. Because ReO₃ has a loosely packed structure, the muffin tins include only one quarter of the unit-cell volume, so one expects the muffin-tin-potential approximation to be poor. When the non-muffin-tin correction is made the d bandwidth increases by roughly a factor of 2. This correction together with some adjustments of the interpolation parameters enabled Mattheiss to fit his results to the optical data of Feinleib *et al.*[5] and the de Haas-van Alphen (dHvA) data of Marcus.[6]

The present study was motivated by the high-pressure dHvA experiment of Schirber *et al.*[7] We have used the Korringa-Kohn-Rostoker (KKR) method for the band calculation in order to avoid the interpolation of bands. In this method the size of the energy matrix is determined by the number of atomic orbitals included in the calculation. We have included the s, p, d states for the Re atoms

and the three O atoms in a unit cell, so the order of the matrix is 36. Therefore, there is no problem in calculating the energy eigenvalues off the symmetry points.

The KKR[8] method has been widely used for the band calculation of pure crystals, i.e., crystals made of one atomic species. The extension of the method to more than one atomic species was formulated by Segall.[9] We have also made use of the Ewald method as formulated by Ham and Segall[10] to carry out the lattice sums in the matrix elements.

We have calculated the energy bands for ReO₃ for the equilibrium-lattice constant[11] and for a lattice constant which is 2% smaller than the equilibrium value to simulate a high-pressure situation. The corresponding pressure may be found from the compressibility data[7] to be 113 kbar. The Fermi surfaces for both the equilibrium lattice and the compressed lattice have been studied. From these results the pressure derivatives of the dHvA frequencies have been calculated and compared with the experiments. Throughout the calculation we have made no adjustment of the potential to fit the bands to experimental data.

CALCULATION

The unit cell of ReO₃ is simple cubic as shown in Fig. 1. The Re atom is located at the origin and the oxygen atoms are located at the face centers and are shared equally with their respective adjacent unit cells.

The crystal potential is constructed along the lines proposed by Mattheiss.[12] The potential consists of the nuclear potential, the Hartree potential constructed from the atomic charge densities of Herman and Skillman,[13] and the full Slater exchange potential.[14] The contributions of the neighboring sites to the potential are summed up by the
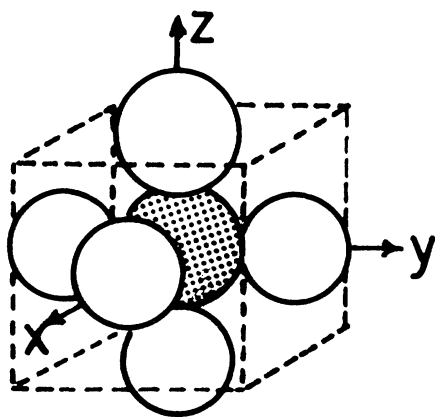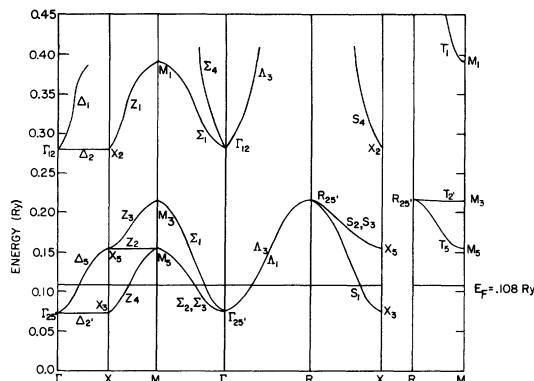

FIG. 2. Electronic energy bands of ReO₃ for the equilibrium lattice. The oxygen bands are below the MT zero.

Löwdin[15] α expansion method. The potential is then spherically symmetrized within the muffin-tin spheres and averaged in the interstitial regions between muffin-tin spheres. Finally, the potential is shifted so that the interstitial region has zero potential.

No spin-orbit corrections have been included here. The spin-orbit coupling reduces many degeneracies at symmetry points and symmetry lines. However, the over-all effect on the dHvA frequencies is to increase the β and γ orbits by about 5% and decrease the α orbit by 5%.

In metals with one atoms per unit cell the muffin-tin (MT) radius is chosen as large as possible so that twice the MT radius is equal to the nearest-neighbor distance. In the case of ReO₃ it is not immediately obvious how the MT radii of the two atomic species should be weighted. Mattheiss chose the ratio for the MT radii $R(\text{Re})/R(\text{O}) = \frac{7}{6}$ in
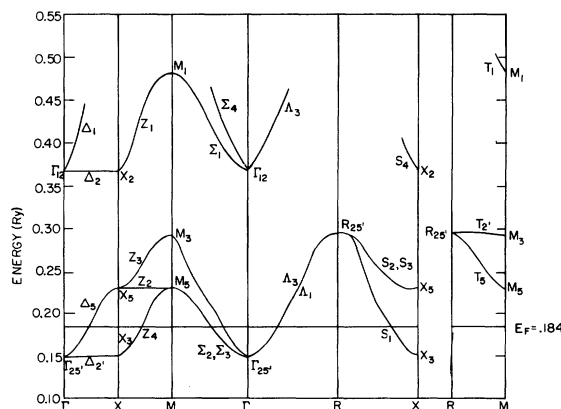

FIG. 1. Unit cell of ReO₃. The open spheres are the oxygens and the dotted sphere is the rhenium.

FIG. 3. Electronic energy bands of ReO₃ for the compressed lattice. The oxygen bands are below the MT zero.
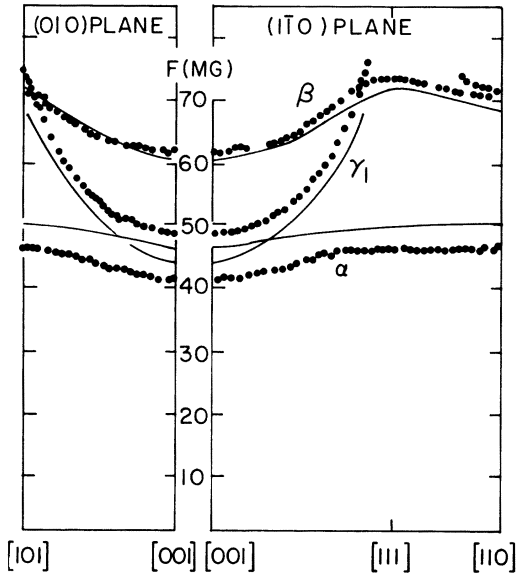
FIG. 4. Variations of the dHvA frequencies between 40 and 80 MG. The solid lines are the calculated values and the dotted lines are the experimental results of Phillips and Shanks.

order to optimize the convergence of the oxygen $2p$ and rhenium $5d$ bands according to an empirical rule of Switendick.[16] We have chosen a larger Re sphere to include more charge in the sphere, 3.8 d electrons instead of 3.3 as in Mattheiss calculation. It turns out that our choice nearly maximizes the total charge, rhenium and oxygen, inside the MT regions. We have tested the effect of different choices of MT radii on the d bandwidth at X. The result was that the width was constant to within 0.002 Ry when the rhenium MT radius is varied from 1.970 to 2.0834 a.u. Therefore, we have taken the rhenium radius to be 2.0834 a.u. and the oxygen radius to be 1.3994 a.u. The MT spheres do not exactly touch on the [100] axis because we have chosen values of the radii that are on the radial mesh. Increasing either the rhenium or oxygen radius to the next point on the radial grid would make the MT spheres overlap in the [100] direction. It turns out that the present volume difference of touching MT radii and nontouching radii is less than 1%. For the 2% compressed lattice the MT radii are chosen so that the rhenium sphere contains 3.6 d electrons. The MT potential for the compressed lattice was generated on a different radial grid than the noncompressed lattice in order to keep the ratio of the MT radii of the two atomic species close to the same value for these two cases; the percent difference of these two ratios is less than 5%. The effect of varying the MT radii for the compressed lattice did not

TABLE I. Lattice parameters and MT radii for the ReO_3 band calculation.

Pressure (kbar)	Lattice parameter (a.u.)	MT radii Rhenium (a.u.)	Oxygen (a.u.)
0	7.0705	2.0834	1.3994
113	6.9290	1.9740	1.3911

alter the width of the d bands more than 0.002 Ry, and hence the pressure derivatives of the Fermi-surface areas would be insensitive to small changes in the MT radii. The lattice parameters and MT radii for the equilibrium and compressed lattice are summarized in Table I.

In setting up the energy matrix we have included s, p, and d states for both rhenium and oxygen, so the order of the matrix is 36. The lattice sums in the structure factor converge well for a choice of 81 reciprocal-lattice vectors and 33 real-space vectors with a Ewald parameter of the value $2(\pi/a)^2$. The energy eigenvalues are determined to within 0.002 Ry for values of wave vectors uniformly distributed on a mesh of 56 points in $\frac{1}{48}$ of the Brillouin zone.

We have not made the non-MT correction because we found that the bands calculated from the MT potential reproduces the experimental Fermi surface quite well. We prefer not to make any other adjustment of the bands so that we can study the pressure shifts of the Fermi-surface geometry without arbitrariness in the calculation.

RESULTS

The energy bands of ReO_3 along the high-symmetry axes for the equilibrium and compressed lattices are shown in Figs. 2 and 3. Only the d bands near the Fermi level are shown. It is interesting to compare our results with those of Mattheiss.[3,4] The shape of our bands resembles very well with the most refined results in Refs.

TABLE II. de Haas-van Alphen frequencies in ReO_3 for high-symmetry directions.

		Frequency in MG Calculated This		Experimental		
Orientation	Branch	work	Ref. 3	Ref. 17	Ref. 6	Ref. 18
[001]	α	46.8	43.1	41.5	41.4	42.0
	γ_1	43.7	49.3	48.8	48.8	49.5
	β	60.5	65.0	61.6	61.8	60.0
	γ_2	92.9	84.5	87.8		
[111]	α	49.8	46.9	46.3	46.1	
	β	72.7	76.2	73.2	73.4	75.0
[110]	α	51.0	47.5	46.3	46.2	47.5
	β	68.5	72.2	70.3	73.5	

TABLE III. Calculated and experimental values for pressure derivatives of cross sections of the Fermi surface of ReO_3.

Cross section	Field Direction	$d \ln F/dp (10^{-4}$ kbar$^{-1})$ Experiment (Ref. 7)	Calculated
α	[001]	4.0 ± 0.3	3.74
	[111]	4.0 ± 0.4	3.64
β	[001]	None	6.42
γ_1	[001]	1.5 ± 0.5	0.64
γ_2	[001]	None	3.76

Scaling prediction ~3.6×10^{-4} kbar^{-1}

3 and 4, but our d band (Γ_{25}' band in Ref. 3) is only half as wide. The reason for this was demonstrated by Mattheiss as due to the MT approximation. The width of our d band compares well with the MT result of Ref. 3. However, our Γ_1 band (not shown) lies above the Γ_{12} bands as obtained by the refined calculations. Thus, although the bandwidth is too narrow, our results give the correct band ordering so that the correct Fermi-surface geometry may be obtained. It is also interesting to note that our oxygen bands are 0.39 Ry below the Fermi level, in fair agreement with the value 0.36 Ry found by Mattheiss.[3]

The Fermi surface of ReO_3 has three sheets corresponding to the three bands which cross the Fermi level. Following the notation of Mattheiss, one labels the three sheets α, β, and γ. The α and β sheets are closed electron surfaces while the γ sheet is multiply connected. These surfaces have been illustrated by Mattheiss[3] and Phillips and Shanks.[17] The Fermi surface for the compressed lattice has the same general features.

From the energy bands we have calculated the dHvA frequencies in high-symmetry directions. The Fermi-surface areas were calculated by first finding the intersections of the three d bands with the Fermi energy along a mesh of 40 planes from $k_z = 0$ to $k_z = \pi/a$, then measuring the enclosed area with a planimeter. The results are compared with the previous calculation and the experimental data

of Marcus,[6] Graebner and Greiner,[18] and Phillips and Shanks[17] in Table II. The over-all agreement is good for an *ab initio* calculation. The largest discrepancy (10%) occurs in the α branch in the [001] direction. The branch β has the largest error of 4% in the [111] direction. The γ_2 orbit is a hole orbit and its frequency has only been calculated here in the [001] direction. Marcus, and Graebner and Greiner did not report this orbit, but the agreement between our calculation and the measurement of Phillips and Shanks is within 6%.

Figure 4 shows the angular dependence of the lower three dHvA frequencies. The data of Phillips and Shanks are plotted on the same graphs. In spite of the systematic errors the calculated curves have the correct shapes.

Schirber *et al.*[7] showed that the dHvA frequencies of ReO_3 do not simply scale with the lattice parameter when the lattice is compressed. The scaling relation assumes that the electron bands do not change shape with compression so that the Fermi surface simply expands together with the Brillouin zone. However, in a real crystal the crystal potential in the interstitial regions is sensitive to the packing of the atoms, and consequently the band shape may change with pressure in subtle ways. Hence, the pressure effect gives a direct test of the accuracy of the method of constructing the crystal potential. Table III shows the comparison between our calculation and the experimental values of the pressure derivatives of the Fermi-surface areas. The agreement is good. Our results indicate clearly the trend that the large, nearly circular α orbit obeys the simple scaling relation, i.e., the corresponding sheet of Fermi surface is insensitive to the changes in the crystal potential, while the smaller, noncircular orbits β and γ are more sensitive to the potential.

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