

The Magnetic Susceptibility of Rhenium Trioxide*

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Magnetic susceptibility measurements have been made on ReO_3 as a function of temperature between 77 and 300 K. The results of the measurements show that ReO_3 has a temperature independent paramagnetism of 0.086×10^{-6} emu/g. A separation of the individual contributions to the measured susceptibility is made and the resultant values are compared with data on cubic sodium tungsten bronzes. The agreement indicates strong similarities between the properties of ReO_3 and Na_xWO_3 as x approaches 1.

Introduction

The red transition-metal oxide ReO_3 which exhibits metallic electrical conductivity has a cubic structure closely related to the perovskite structure observed in the sodium tungsten bronzes. Similarities in the properties of ReO_3 and the sodium tungsten bronzes have been pointed out by Sleight and Gillson (1), Graebner and Greiner (2), and Ferretti et al. (3). In particular, one would expect ReO_3 to have properties very similar to those of cubic Na_xWO_3 as x approaches 1. Rhenium oxide, however, has been reported to be diamagnetic by Ferretti et al. (3) while the cubic Na_xWO_3 compounds are paramagnetic (4). Recently a paper by Quinn and Neiswander (5) reported a weak paramagnetism in ReO_3 .

In light of the above disagreement between investigators and the similarity between ReO_3 and the sodium tungsten bronzes it seemed desirable to make an extensive study of the magnetic susceptibility of ReO_3 and its relationship to the susceptibility of Na_xWO_3 . It was also the hope that the study would help to increase the understanding of the properties of the tungsten bronzes.

Experimental Procedure and Results

Starting material for the measurements was purified ReO_3 powder purchased from City

Chemical Corp. of New York. Crystalline material (grain size approximately 1 mm) was obtained by iodine vapor transport of the commercial material. The preparation of ReO_3 single crystals by this method has been reported by Ferretti et al. (3) and Graebner and Greiner (2).

Rhenium trioxide powder and enough iodine to produce a partial pressure of 300 Torr at the transporting temperature were placed in a clean quartz tube 25 cm long and 5 cm in diameter. The tube was evacuated to 10^{-4} Torr and sealed off. The transport was carried out in a horizontal split-tube furnace with a temperature gradient along the length of the quartz tube of 10°C . The end of the quartz tube with the starting material was placed in the hot zone of the furnace. The temperature of the hot end of the tube was maintained at 385°C and the temperature of the cooler end was kept at 375°C . After a transport time of 14 days, deep red cubes of ReO_3 up to 4 mm on a side were found deposited on the cooler end of the tube.

The crystals were removed from the quartz tube and washed several times in absolute alcohol to remove any iodine residue. A complete mass spectrographic analysis of the ReO_3 crystals is given in Table I along with analysis of the starting material. No iodine was detected in the transported crystals. The detection limit by mass spectroscopy for iodine is much less than 1 ppm. Of particular importance to magnetic susceptibility measurements was the decrease in magnetic impurities after vapor transport.

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TABLE I
ANALYSIS OF ReO_3 BY MASS SPECTROSCOPY

Impurity	Starting material (ppm)	Trans-ported material (ppm)	Impurity	Starting material (ppm)	Trans-ported material (ppm)
Be	≤1.0	≤0.9	Cr	20	2.0
B	≤30.0	≤50.0	Mn	5.0	0.2
F	4.0	0.3	Fe	200	0.6
Na	370	30	Co	10	0.1
Mg	20	ND*	Ni	7.0	0.06
Al	7.0	3.0	Cu	60	0.5
Si	50	10	Zn	40	0.9
P	1.0	3.0	Ga	≤0.2	ND
S	≤50	≤10	As	1.0	0.4
Cl	20	50	Y	0.6	40.0
K	40	2.0	Mo	1.0	5.0
Ca	7.0	5.0	Cd	≤0.9	ND
Sc	≤4.0	≤4.0	Pr	≤1.0	ND
Ti	≤5.0	≤6.0	Pb	3.0	ND
V	200	0.3			

* Not detected.

The following elements were looked for but not detected.

Ge	Ru	Sb	Ce	Dy	W	Tl
Se	Rh	Te	Nd	Er	Os	Bi
Br	Pd	I	Sm	Yb	Ir	Th
Rb	Ag	Cs	Eu	Lu	Pt	U
Sr	In	Ba	Gd	Hf	Au	
Zr	Sn	Lu	Tb	Ta	Ag	

The crystals of ReO_3 were checked for phase purity and the lattice constant was determined with the use of a standard Debye-Scherrer X-ray camera. The lattice constant as obtained from the average of three independent determinations was 3.7455 ± 0.0003 Å. The lattice constant as reported by Magnéli (6) for material of undefined purity was 3.7510 ± 0.0005 Å.

Electrical resistivity measurements were made on rectangular single crystals using a standard four-probe method. A value of $9.5 \pm 0.2 \times 10^{-6}$ ohm-cm was obtained at 300 K. The error is due in large part to the uncertainty in the measurement of the dimensions of the small samples. Ferretti et al. (3) and Feinleib et al. (7) indicate similar values while Marcus (8) reports a higher value of 1.82×10^{-5} ohm-cm.

The resistivity ratio $\rho_{300}/\rho_{4.2}$ was also measured as a further indication of the quality of the crystals. A ratio of about 500 was obtained which is very high when compared with the best resis-

tivity ratios of less than 10 obtained for the cubic sodium tungsten bronze crystals.

The magnetic susceptibility was measured by the Faraday method. The room temperature data were obtained in an apparatus consisting of a six-inch Varian magnet with constant $H(dH/dz)$ pole pieces and an Ainsworth 24N single-pan balance. A draft shield surrounding the suspension was added below the balance and access was provided in the magnet gap for the placement of the sample. The optical scale of the balance was calibrated against a 100 mg NBS class *M* weight and the magnet constants were adjusted to the values given by Bates (9) for pure water and mercury of -0.722×10^{-6} emu/gm and -0.167×10^{-6} emu/gm, respectively. The correction for the volume of air displaced by the sample was based on the value of 0.03×10^{-6} emu/cm³ multiplied by the density of ReO_3 .

The results of the room temperature measurements on vapor transport purified ReO_3 are listed in Table II. Samples VT-1 and VT-3 consisted of several polycrystalline platelets, one-fourth to one square cm in area by one to two mm in thickness, stacked directly on the suspension platform. Sample VT-2 was selected from the smaller pieces removed from the vapor transport apparatus and was placed in a Teflon container. The susceptibility of the empty Teflon container was measured and a field and temperature independent (77 to 300 K) value of -0.382×10^{-6} emu/gm was obtained.

No systematic field dependence to the susceptibility of ReO_3 was observed so the apparent susceptibilities were averaged over the five measured field strengths. The uncertainties shown in Table II are the root-mean-square deviations from the average value. The uncertainty value for the Teflon container has been

TABLE II
THE ROOM TEMPERATURE MASS SUSCEPTIBILITY OF VAPOR-TRANSPORT PURIFIED ReO_3

Sample number	Sample mass (g)	Mass susceptibility ($\times 10^6$ emu/g)
VT-1	2.4728	0.085 ± 0.002
VT-2	1.4617	0.088 ± 0.005
VT-3	2.4092	0.085 ± 0.003
Weighted average		0.086 ± 0.002

added to the value for sample VT-2. The results given in Table II show no detectable inhomogeneity between samples; therefore, an average value, weighted by the respective uncertainties of the three samples, is taken as the mass susceptibility of ReO_3 .

The temperature dependence of the susceptibility of sample VT-2 was measured in an apparatus described previously (4). The motor-generator magnet current supply, however, has been replaced with a Hewlett-Packard 6269A constant current regulator for better stability and more ripple-free operation. The apparent susceptibilities were measured at six field strengths and were again arithmetically averaged. The temperature was measured with a copper *vs.* constantan thermocouple and equilibration times were chosen to ensure sample temperatures within ± 1 K of the given values. The nine temperatures between 298 and 77 K were maintained at ± 0.1 K throughout each run. These results are listed in Table III.

Sleight et al. (10) report finding no superconducting transition in ReO_3 down to 1.3 K. To further characterize the material used in this investigation a small gelatin encapsulated sample was measured in a mutual inductance bridge from 4.2 to 1 K. A constant paramagnetic signal was observed. However, calibration of the apparatus to obtain the magnitude of the susceptibility was not performed.

Discussion

In general, one can write the total magnetic susceptibility as

$$\chi = \chi_c + \chi_{\text{VV}} + \chi_e,$$

where χ_c is the Langevin diamagnetism of the ion cores, χ_{VV} is the Van Vleck temperature-independent orbital paramagnetism and χ_e is the susceptibility of the conduction electrons.

The electrical conductivity and temperature-independent paramagnetism of ReO_3 which were found in this investigation are in accord with the behavior measured previously on the metallic sodium tungsten bronzes (4). It was found that the susceptibility of Na_xWO_3 in the range $0.49 \lesssim x \lesssim 0.85$ increased with increasing sodium concentration and good agreement was obtained between the observed and calculated susceptibilities with a model which assumed a lattice composed of WO_6 octahedra with a random distribution of interstitial sodium ions each

TABLE III
MASS SUSCEPTIBILITY AS A FUNCTION OF TEMPERATURE FOR SAMPLE VT-2

Temperature (°K)	Mass susceptibility ($\times 10^6$ emu/g)
298	0.088
249	0.088
195	0.086
178	0.086
167	0.088
134	0.086
106	0.088
82	0.088
77	0.090

contributing one electron to the conduction band. Similarly, the experimental absence of an unpaired spin in the structurally related ReO_6 octahedra indicates the availability of one conduction electron per unit cell which corresponds to the electron concentration expected for NaWO_3 . With the exception of the diamagnetic contribution from the core electrons of the sodium ions, therefore, comparable susceptibility values might be anticipated for these two materials. Because it was not possible to obtain sufficient NaWO_3 to make direct measurements, a linear least-squares fit of the bronze data was made and an extrapolation to $x = 1$ gave a value of $16 \pm 3 \times 10^{-6}$ emu/mole. Subtraction of the value for the sodium ion cores (11) results in a value of $22 \pm 3 \times 10^{-6}$ emu/mole for the combined susceptibility of the WO_3 lattice and the conduction electrons. This agrees remarkably well with the molar susceptibility of 20×10^{-6} emu/mole obtained for the three ReO_3 samples.

Since WO_3 is an insulator (therefore $\chi_e = 0$), one can obtain the orbital paramagnetism term, χ_{VV} , directly from the difference between the experimentally determined magnetic susceptibility and the sum of the individual ion core terms. The core values of $\text{W}^{+6} = -13 \times 10^{-6}$ and $\text{O}^{-2} = -12 \times 10^{-6}$ and the experimental value of -14×10^{-6} reported by Greiner et al. (4), therefore yield an orbital paramagnetism term, $\chi_{\text{VV}} = 35 \times 10^{-6}$ for WO_3 .

One would expect the orbital paramagnetism term to be of about the same magnitude for NaWO_3 and ReO_3 since they are structurally

related to WO_3 . Using core terms of -5×10^{-6} for Na^+ and -12×10^{-6} for Re^{+7} and an assumed χ_{VV} of 35×10^{-6} we calculate values of 33×10^{-6} and 35×10^{-6} for the values of χ_e for NaWO_3 and ReO_3 , respectively.

The magnetic susceptibility of the conduction electrons can be written as

$$\chi_e = \chi_p + \chi_d,$$

where χ_p is the spin paramagnetism and χ_d is the diamagnetic contribution arising from the translational motion of the electrons in a magnetic field.

A value for χ_d for ReO_3 was not calculated but it seems reasonable to assume a value similar to that obtained for Na_xWO_3 . In any case, χ_d is expected to be small since Greiner et al. (4) found that χ_d for the sodium tungsten bronzes is never greater than 8% of χ_p . We can therefore assume that the values obtained above for χ_e of NaWO_3 and ReO_3 are lower limits for χ_p . Since χ_d is expected to be 8% or less of χ_p , χ_p is not more than 8% greater than χ_e for either material.

Several authors (12, 13) have discussed the spin susceptibility in transition metals. They show that the spin susceptibility can be written as

$$\chi_p = 2\mu_B^2 N(0) \left[\frac{1}{1 - N(0)V} \right],$$

where μ_B is the Bohr magneton, $N(0)$ is the bare density of states at the Fermi surface and V is the spin interaction. The term,

$$\frac{1}{1 - N(0)V}$$

takes account phenomenologically of electron correlations in d -band materials and is referred to as an enhancement or Stoner factor. One can obtain the magnitude of the Stoner factor from the ratio, χ_p/χ_e , where γ is obtained from the electronic specific heat

$$C_e = \gamma T.$$

Keller (14) has recently measured the specific heat of ReO_3 at low temperatures. He obtained a value for γ of 2.85 mJ/mole deg². Similarly, a reasonable extrapolation of the specific heat data on Na_xWO_3 reported by Vest et al. (15) to $x = 1$ gives a value of 3.05 mJ/mole deg² for NaWO_3 . Using these experimental values for γ and the calculated values for χ_p we obtain a Stoner factor of 1.1 for both ReO_3 and NaWO_3 . The NMR results of Narath and Barham (16)

show that the conduction-band states of ReO_3 and Na_xWO_3 are identical and predominantly d -like. The value of 1.1 is therefore unexpected since the Stoner factor is found to be significant in most conducting d -band materials (13).

Summary

Measurements of the magnetic susceptibility of high purity ReO_3 show that the compound has a temperature-independent paramagnetism. The individual contributions to the measured susceptibility can be separated and compared with the values for Na_xWO_3 . The contribution to the magnetic susceptibility from electron correlations appears to be small in both ReO_3 and Na_xWO_3 .

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