real situation is more complex than this. Europium or its diamagnetic replacement can occupy only discrete lattice sites; on dilution, there is no real increase in Eu–Eu spacing but only a decrease in the probability that a neighboring site is occupied by another europium. Hence, the observed change in sign of the magnetic interaction is probably due to the increasing electron density brought about by substituting trivalent lanthanum for divalent europium. As the population of the conduction band increases, the Fermi wave number increases, and the effect is as if the polarization wave were swept past a neighboring lattice site to oscillate the sign of the magnetic ordering interaction.

Matthias[12] has attributed the ferromagnetism observed for EuB_6 to magnetic polaron formation as predicted by Nagaev[13] for a semiconducting antiferromagnet. Unfortunately, available conductivity data and Flodmark's band calculation do not unambiguously establish that EuB_6 is nonmetallic or semiconducting. The complication in the present investigation is that dilution of EuB_6 by lanthanum substitution not only increases the average spacing between europium ions but also increases the conduction electron density. Experiments with Gd dilution and with Yb dilution to separate the two effects of changing electron density and magnetic dilution are now in progress.

Acknowledgment.—This research was sponsored by the U. S. Air Force Office of Scientific Research and was supported in part by NSF and ARPA. The manuscript was written at the Laboratoire d'Electrostatique et de Physique du Metal, CNRS-Rayons X, Grenoble, France. The hospitality of Dr. E. F. Bertaut and the support of the John Simon Guggenheim Memorial oundation to M. J. S. are gratefully acknowledged.

[12] B. T. Matthias, *Phys. Lett. A*, **27**, 511 (1968).

[13] E. L. Nagaev, *Zh. Eksp. Teor. Fiz.*, **54**, 228 (1968).

Contribution from the Baker Laboratory of Chemistry,
Cornell University, Ithaca, New York 14850

Low-Temperature Magnetic Susceptibility of Gadolinium and Terbium Tungsten Oxide Bronzes

By Joseph R. Shannon and M. J. Sienko*[1]

Received July 27, 1971

The metallic tungsten bronzes, M_xWO_3, are of special interest in solid-state chemistry because they are nonstoichiometric compounds in which the identity of dopant metal M and its level of concentration in the host matrix WO_3 can be varied over wide limits so as to permit study of the effect of electron concentration on physical properties.[2] In particular, when M is a rare earth element, one has a magnetic bronze, in which the interaction of conduction electrons and magnetic moments can be investigated. When x is large enough, the tungsten bronzes are approximately cubic with a unit cell in which there are W atoms at cube corners, O atoms near midpoints of cube edges, and fractional occupancy by M atoms of the cube center position. The metallic properties are ascribed to transfer of valence electrons from the M atoms to conduction bands made of W 5d t_{2g} orbitals with admixture of O p_π character.[3]

Ostertag[4] was the first to prepare tungsten bronzes in which the M atoms were rare earth metal atoms. For both europium and gadolinium he found that the structures were cubic over the range $0.085 < x < 0.18$. Subsequent work[5] showed that the resistivity was small, increased linearly with rising temperature, and had a temperature coefficient comparable to that of a metal. Attempts in this laboratory to measure Hall voltages on these crystals have proved unsuccessful, partly because of the odd pyramidal shape of the crystals; however, it seems almost certain that each rare earth atom contributes three electrons to the conduction band. Magnetic susceptibility measurements, in the range 77–300°K, had led Ostertag to conclude that the rare earth ions are indeed triply charged.

Ostertag[6] has also succeeded in making a uranium–tungsten bronze, and he has measured its magnetic susceptibility to a much lower temperature, down to 4.2°K. Although behavior above 60°K is Curie–Weiss ($\chi = C/(T - \Theta)$), with an extrapolated Weiss temperature $\Theta = -170°$, a clear minimum was also observed in the reciprocal susceptibility *vs.* temperature corresponding to a Néel temperature of about 30°K. Dilution of the uranium with diamagnetic thorium did not change the magnetic parameters, so it was assumed that the magnetic coupling was due to indirect exchange through conduction electrons. The current investigation was undertaken to see if similar indirect exchange might also occur at very low temperatures in the rare earth–tungsten bronzes. Gadolinium was chosen because of its high, spin-only magnetic moment; terbium was also investigated to see if there is an effect of an f-orbital component.

Experimental Section

Materials.—$Gd_{0.15}WO_3$ and $Tb_{0.15}WO_3$ were prepared by solid-state reaction according to the method of Ostertag.[4] A mixture composed of rare earth metal oxide, tungsten trioxide, and tungsten metal was ground in a ball mill under a nitrogen atmosphere for 8 hr. It was then heated under argon at 1100° for 24 hr, quenched, reground, and reheated. X-Ray diffraction patterns showed only the cubic tungsten bronze phase present. Starting materials were 99.9% Gd_2O_3 from American Potash and Chemical Co., "Specpure" Tb_4O_7 from Johnson Matthey Co., and highest purity W and WO_3 from Fisher Chemical Co.

Measurements.—Magnetic susceptibilities were measured over the range 1.5–300°K using the Gouy method with the apparatus previously described.[7] Samples were packed in 0.4-cm diameter silica tubes up to a height of about 20 cm. The temperature cycle was done in two stages, one using liquid nitrogen alone and the other using liquid helium. Data on descending and ascending temperature were reproducible to better than 1%. Magnetic field was varied from 300 to 2000 Oe at each temperature. Except at the very lowest temperature, plots of susceptibility *vs.*

---

(1) To whom correspondence should be addressed.

(2) For reviews on the tungsten bronzes see M. J. Sienko, *Chem. Soc., Spec. Publ.*, **No. 22**, 429 (1967); P. G. Dickens and M. S. Whittingham, *Quart. Rev., Chem. Soc.*, **22**, 30 (1968).

(3) J. C. Gulick and M. J. Sienko, *J. Solid State Chem.*, **1**, 195 (1970).

(4) W. Ostertag, *Inorg. Chem.*, **5**, 758 (1966).

(5) W. Ostertag and C. V. Collins, *Mater. Res. Bull.*, **2**, 217 (1967).

(6) W. Ostertag, *Inorg. Chem.*, **8**, 1373 (1969).

(7) J. B. Sohn, Ph.D. Thesis, Cornell University, 1965.

reciprocal field were flat to 1%. Fields were calibrated with standard solutions of nickel chloride and with $HgCo(NCS)_4$.

Results and Discussion

Figure 1 shows as a function of temperature the observed reciprocal molar susceptibility of $Gd_{0.15}WO_3$ and of $Tb_{0.15}WO_3$. In neither case has there been any correction made for diamagnetism of the rare earth ion and the host WO_3 or for the Pauli paramagnetism of the electron gas. As Ostertag has indicated, these corrections almost cancel each other, and, in any case, the observed susceptibilities are so large that either correction would be insignificant. Table I shows the observed magnetic parameters as referred to a Curie–Weiss law $\chi = C/(T - \Theta)$ with the effective magnetic moment $\mu_{\text{eff}} = (3kC/N)^{1/2}$. Calculated moments for comparison are obtained from $\mu = g[J(J + 1)]^{1/2}$ for the ground states of the free ions—*viz.*, $^8S_{7/2}$ for Gd^{3+} ($4f^7$, $g = 2$, $S = 7$, $L = 0$, $J = {}^7/_2$) and $^7F_6$ for Tb^{3+} ($4f^8$, $g = 1.5$, $S = 3$, $L = 3$, $J = 6$). The very small values of the Weiss parameter Θ and the excellent agreement between the observed μ_{eff} and the calculated μ indicate that each of the compounds is magnetically ideal. The agreement observed is about as good as that observed for the magnetically dilute hydrated sulfates (*e.g.*, in $Gd_2(SO_4)_3 \cdot 8H_2O$ the observed μ_{eff} is 7.91 BM and Θ is about 2°; in $Tb_2(SO_4)_3 \cdot 8H_2O$, μ_{eff} is 9.50 BM and $\Theta = 16°$).

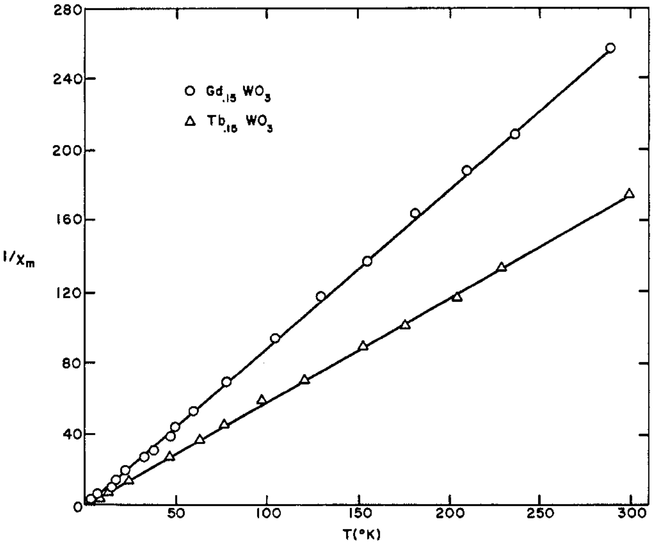

Figure 1.—Reciprocal molar susceptibility *vs.* temperature for gadolinium–tungsten bronze and terbium–tungsten bronze.

TABLE I

MAGNETIC PARAMETERS FOR GADOLINIUM- AND TERBIUM-TUNGSTEN BRONZES

Compn	Θ, °K	μ_{eff}, BM	μ_{calcd}, BM
$Gd_{0.15}WO_3$	2 ± 2	7.90	7.94
$Tb_{0.15}WO_3$	5 ± 2	9.76	9.72

That the rare earth–tungsten bronzes should show such close fit to ideal Curie behavior and that this fit should hold to such very low temperature is not entirely expected. Granted that in $Gd_{0.15}WO_3$ and $Tb_{0.15}WO_3$ the Gd^{3+} and Tb^{3+} are so far apart (7.2 Å, on the average) that direct dipolar interaction is negligible, there still remains the possibility of the Ruderman–Kittel indirect exchange interaction through the conduction electrons.[8] Since the polarization of an itinerant electron changes sign in oscillating manner as the distance from a magnetic atom increases, one would expect moment alignment of neighboring magnetic ions either parallel (ferromagnetic) or antiparallel (antiferromagnetic) depending on the distance from the original magnetic ion.

This kind of analysis, however, is valid only if the conduction electrons use the atomic orbitals of the magnetic ion, so that dipole interaction between the itinerant electrons and the localized moment can occur. If, for example, in Gd_xWO_3, the conduction electrons do *not* use gadolinium orbitals but are confined to the W 5d t_{2g}–O p_π network, then the interaction may be too weak to align the localized moments either parallel or antiparallel. In general, 4f orbitals are too highly localized to contribute appreciably to conduction band states; also, the probability of exciting a 4f electron into a conduction band (5d or 6s) is not very likely.

The fact that Ostertag found a Néel temperature and antiferomagnetic coupling for uranium–tungsten bronze suggests that the case of uranium is different. One possible reason for this is that the uranium magnetic moment comes from 5f orbitals, which have larger spatial extent than 4f and hence may participate in conduction band states; another possibility is that the 5f orbital which carries the magnetic moment is close enough in energy to the 6d to be easily excited to it. In such case the spatial extent of the localized moment would be even greater and interaction with the conduction band more effective.

Acknowledgment.—This research was sponsored by the U. S. Air Force Office of Scientific Research and was supported in part by NSF and ARPA. The manuscript was written at the Laboratoire d'Electrostatique et de Physique du Metal, CNRS-Rayons X, Grenoble, France. The hospitality of Dr. E. F. Bertaut and the support of the John Simon Guggenheim Memorial Foundation to M. J. S. are gratefully acknowledged.

---

(8) M. A. Ruderman and C. Kittel, *Phys. Rev.*, **96**, 99 (1954).

CONTRIBUTION FROM RESEARCH AND DEVELOPMENT,
SUN OIL COMPANY, MARCUS HOOK, PENNSYLVANIA 19061,
AND THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF DELAWARE,
NEWARK, DELAWARE 19711

Far-Infrared Spectra (40–400 Cm^{-1}) of Palladium(II) Isothiocyanate and Isoselenocyanate Complexes Undergoing Linkage Isomerization in the Solid Phase and of Related Complexes

BY JAMES L. LAUER,*[1a] MELVIN E. PETERKIN,[1a] JOHN L. BURMEISTER,[1b] KAREN A. JOHNSON,[1b] AND JOHN C. LIM[1b]

Received August 2, 1971

Linkage isomerization is a process still incompletely understood. A pair of true linkage isomers is difficult to obtain since, in general, one form is much more

---

(1) (a) Sun Oil Co. (b) University of Delaware.