Crystal Structure and Magnetic Properties of Sm$_2$ReO$_5$

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Crystals of disamarium rhenium (IV) pentoxide, Sm$_2$ReO$_5$, were obtained by subsolidus reaction of samariumsesquioxide and rheniumdioxide (ratio 1:1) in sealed Pt 10Rh tubes at 1673 K. The structure was determined by single-crystal X-ray diffraction. Sm$_2$ReO$_5$ crystallizes in the tetragonal system with unit cell dimensions $a = 8.646(3)$ Å and $c = 5.747(2)$ Å and space group P4/n (no. 85) with $Z = 4$. The structure consists of isolated Re$_2$O$_8$ groups and chains of edge-sharing Sm$_4$O tetrahedra. The Re$_2$O$_8$ groups and the (Sm$_4$O) chains are interconnected by common oxygen atoms to form a three-dimensional network. Each Re$_2$O$_8$ group is composed of a pair of rhenium each surrounded by four oxygens with a short Re–Re distance of 2.251(1) Å indicating a metal–metal bond. Rhenium has the formal oxidation state of $+4$. The observed magnetizations in the temperature range $1.8 < T < 100$ K exhibits antiferromagnetic ordering below 2.4(1) K and obey a Curie–Weiss law modified by a temperature-independent Van Vleck paramagnetism of samarium (3+) for $T > 4.5$ K. © 1997 Academic Press

INTRODUCTION

The occurrence of rhenium in a wide range of oxidation states leads to a rich and interesting coordination chemistry that is well illustrated in both binary and ternary oxides. The structures of several ternary rare-earth rhenium oxides exhibiting rhenium–rhenium bonds are known. These pairs are coordinated by oxygen in two different ways. Re$_2$O$_{10}$ groups were discovered in the compound La$_4$Re$_6$O$_{19}$ (1, 2), in which two ReO$_6$ octahedra share a common edge. A Re$_2$O$_8$ unit was found in La$_4$[Re$_2$]O$_{10}$ (3) where the rhenium pairs are surrounded by a square prismatic arrangement of oxygen atoms. Both types of dimeric units are seen in La$_6$Re$_4$O$_{18}$ (4). In Dy$_5$Re$_2$O$_{12}$ (5), BiRe$_2$O$_6$ (6), and La$_4$Re$_6$O$_{19}$ (1, 2), the ReO$_6$ octahedra share corners to form chains, layers, and a three-dimensional network, respectively. Isolated Re$_2$O$_{10}$ groups exist in La$_6$Re$_4$O$_{18}$ (4), Nd$_4$Re$_2$O$_{11}$ (7), and La$_3$Re$_2$O$_{10}$ (8). Furthermore in PbRe$_2$O$_6$ (9) exists the Re$_2$O$_{10}$ unit without metal–metal bonding. The Bravais lattice types of compounds with the nominal stoichiometry Ln_2ReO$_5$ are reported for $Ln =$ La, Nd, Sm, Gd, Dy, Y, Er, and Yb (10). Accordingly, for $Ln =$ Sm and Gd a primitive tetragonal unit cell with $Z = 4$ has been suggested, but neither a specific space group nor further structural details are given there. Single-crystal X-ray diffraction on La$_2$ReO$_5$ revealed a body-centered tetragonal structure which is closely related to the fluorite type (11). In contrast to the square prismatic oxygen coordination of both the Re–Re pairs and the La ions, an antiprismatic coordination is reported for the Re–Re pairs and the Eu ions in Eu$_2$ReO$_5$, derived from X-ray diffraction on a twinned crystal, using space group P4/n (12). Furthermore it was claimed that the compounds Ln_2ReO$_5$ with $Ln =$ Sm, Eu, and Gd would be isotypes, but atomic parameters and connectivity schemes are lacking in literature for all these compounds.

In this paper we report about the structure determination of Sm$_2$ReO$_5$ based on single-crystal X-ray diffraction data and compare the refined structure with that known of La$_2$ReO$_5$ and with the reported structure elements in Eu$_2$ReO$_5$. Furthermore we report about the magnetic properties of this compound. This is an important point to elucidate whether the rhenium–rhenium bonds are metallic bonds.

EXPERIMENTAL

The synthesis of Sm$_2$ReO$_5$ single crystals was carried out by subsolidus reaction of a stoichiometric mixture of reagent grade samariumsesquioxide (Sm$_2$O$_3$, Aldrich 99.99%) and rheniumdioxide (ReO$_2$, Alfa 99.99%) in the ratio 1:1. All reactants were intimately mixed in an agate mortar under acetone and sealed into a Pt 10Rh tube under argon atmosphere. The sample was heated in a tube furnace in argon atmosphere with a ramping rate of 300 K/h to 1673 K and kept for 12 h. Afterward it was cooled down with 180 K/h to room temperature. The argon atmosphere was used as a protection measure.

On opening the tube a single phase of not very well-developed dark red crystals was obtained. The mean diameter of a crystal was as large as 0.05 to 0.15 mm. The

TABLE 1
Details of X-Ray Single-Crystal Data Collection and Structure Refinement

Diffractometer: STOE-STADI 4	Radiation:Mo K_α, $\lambda = 0.71069$ Å
Fine-focus sealed tube	Graphite monochromator
Detector: Scintillation counter	Pulse-height discrimination
Scan: $\Theta/2\Theta$	Cell parameters from 40 reflections ($63.3° \leq 2\Theta \leq 69.8°$)
Crystal size: $0.05 \times 0.06 \times 0.07$ mm	Crystal habit: spherical
Crystal color: red	Temperature: 298 K
$h = 0 \rightarrow 12$	2455 measured reflections ($6° \leq 2\Theta \leq 60°$)
$k = -12 \rightarrow 12$	637 independent reflections [$R_{int} = 0.1027$]
$l = -8 \rightarrow 6$	
Absorption correction: ψ scan	Max. and min. transmission: 0.0676 and 0.0211
Refinement method (44 parameters)	Full-matrix least-squares on F^2
GooF = $S = 1.157$	$\Delta\rho_{max} = 5.29$ eÅ^{-3}, $\Delta\rho_{min} = -1.88$ eÅ^{-3}
Final R indices 577 [$F > 4\sigma$]	$R_1 = 0.0284$, w$R_2 = 0.0508$
R indices 637 (all data)	$R_1 = 0.0340$, w$R_2 = 0.0535$
Extinction correction: Zachariasen	Extinction coefficient: $0.0171(5) \times 10^{-4}$
$\mu = 55.5$ mm^{-1}	$D_x = 8.765$ Mg/m^3
Atomic scattering factors from:	Int. Tables Vol. IV, Tables 2.2B and 2.3.1
Structure refinement: SHELXS-86 (13), SHELX-93 (14)	

sample itself was checked microscopically (optical and REM) as well as by EDX (Sm : Re ratio = 2 : 1) and X-ray diffraction. The details of the X-ray single-crystal data collection and structure refinement are summarized in Table 1.

In order to determine the magnetic properties, magnetization measurements were performed in the temperature range from 1.8 to 100 K using a SQUID (QUANTUM DESIGN) with a field strength of 1 T.

RESULTS

Positional parameters and selected interatomic distances for Sm$_2$ReO$_5$ are listed in Table 2 and Table 3, respectively. The crystal structure of Sm$_2$ReO$_5$ is displayed in Figs. 1–3. The formal oxidation state of rhenium in this compound is +4.

The structure of Sm$_2$ReO$_5$ contains isolated Re$_2$O$_8$ groups, staggered along the [001] direction (Fig. 3a), which

TABLE 2
Atomic and Thermal Parameters for Sm$_2$ReO$_5$ at 298 K as Derived from Single-Crystal X-Ray Diffraction

Space group	a (Å)	b (Å)	c (Å)	V (Å^3)	Z
$P4/n$	8.646(3)	8.646(3)	5.747(2)	429.6(3)	4
Atom	Position	x	y	z	U_{eq} (Å^2)
Sm(1)	8(g)	0.40051(5)	0.60796(5)	0.24951(6)	0.0058(1)
Re(1)	2(c)	0.25	0.25	0.15099(10)	0.0047(2)
Re(2)	2(c)	0.25	0.25	0.54263(10)	0.0049(2)
O(1)	2(a)	0.25	0.75	0.00	0.005(2)
O(2)	2(b)	0.25	0.75	0.50	0.003(2)
O(3)	8(g)	0.1581(6)	0.4492(7)	0.1030(10)	0.010(1)
O(4)	8(g)	0.3406(6)	0.4482(6)	0.6019(10)	0.008(1)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Sm(1)	0.0066(2)	0.0062(2)	0.0046(2)	0.0002(2)	0.0005(2)	0.0009(2)
Re(1)	0.0055(2)	0.0055(2)	0.0031(2)	0	0	0
Re(2)	0.0057(2)	0.0057(2)	0.0031(2)	0	0	0
O(1)	0.005(3)	0.005(3)	0.005(4)	0	0	0
O(2)	0.004(3)	0.004(3)	≤ 0.005	0	0	0
O(3)	0.009(2)	0.009(3)	0.012(3)	0.003(2)	0.002(2)	0.000(2)
O(4)	0.006(2)	0.011(3)	0.008(2)	$-0.004(2)$	$-0.002(2)$	0.000(2)

TABLE 3
Bond Lengths (Å) in Sm_2ReO_5.

Sm(1)–O(1)	2.293(1)
Sm(1)–O(2)	2.296(1)
Sm(1)–O(3)	2.643(6)
Sm(1)–O(3b)	2.445(6)
Sm(1)–O(3d)	2.485(5)
Sm(1)–O(4)	2.506(6)
Sm(1)–O(4a)	2.444(5)
Sm(1)–O(4c)	2.547(5)
Re(1)–O(3)	1.917(6)
Re(2)–O(4)	1.915(6)
Re(1)–Re(2)	2.251(1)

Note. Symmetry equivalent pairs are not included. a: $1 - x, 1 - y, 1 - z$; b: $1 - y, x + \frac{1}{2}, -z$; c: $1 - y, x + \frac{1}{2}, 1 - z$; d: $y, \frac{1}{2} - x, z$.

are interconnected by samarium atoms to form a three-dimensional framework (Fig. 3b). Two crystallographically independent rhenium sites exist in this structure type within a Re_2O_8 unit. This group is composed of a pair of rhenium each surrounded by four oxygens to form a quadratic pyramid. The oxygens of these two independent rhenium atoms are arranged in a staggered conformation (Fig. 2). The rhenium–rhenium distance within this unit (2.251 Å) is much shorter than in the solid metal itself. The samarium atoms

form Sm_4O tetrahedra with the two independent oxygen atoms O(1) and O(2). These tetrahedra are linked to each other via common oxygens to form edge-sharing chains in the [001] direction. Furthermore four of these chains of Sm_4O tetrahedra are linked to the Re_2O_8 unit by bridging with O(3) and O(4) oxygen. They build up a channel system in which the Re_2 units are located (Fig. 1). The coordination of the samarium atoms by the 8 oxygens given in Table 3 can also be described as quadratic antiprismatic, but in contrast to the rhenium–rhenium pair pronounced distortions are observed. The geometries within both "quadratic" layers and the plane equations are summarized in Tables 4a and 4b. Both layers are tilted with respect to each other by an angle of 4.79(0.22)°. In contrast to the quadratic antiprismatic coordination of both the Sm atoms and the rhenium–rhenium pairs in Sm_2ReO_5, quadratic prismatic formations exist in La_2ReO_5 (11). This difference has also been reported for Eu_2ReO_5 (12), but the postulated isotype of Sm_2ReO_5, Eu_2ReO_5, and Gd_2ReO_5 still cannot be confirmed by us because of lacking structural details in literature for the latter two compounds.

The inverse observed magnetization per mole is shown in Fig. 4 together with a fit according to a Curie–Weiss law modified by an additional temperature-independent contribution M_0. The best fitting parameters are refined to $C = 516.5$ emu K/mol, $\Theta = -3.36$ K, and $M_0 = 9.66$ emu/mol.
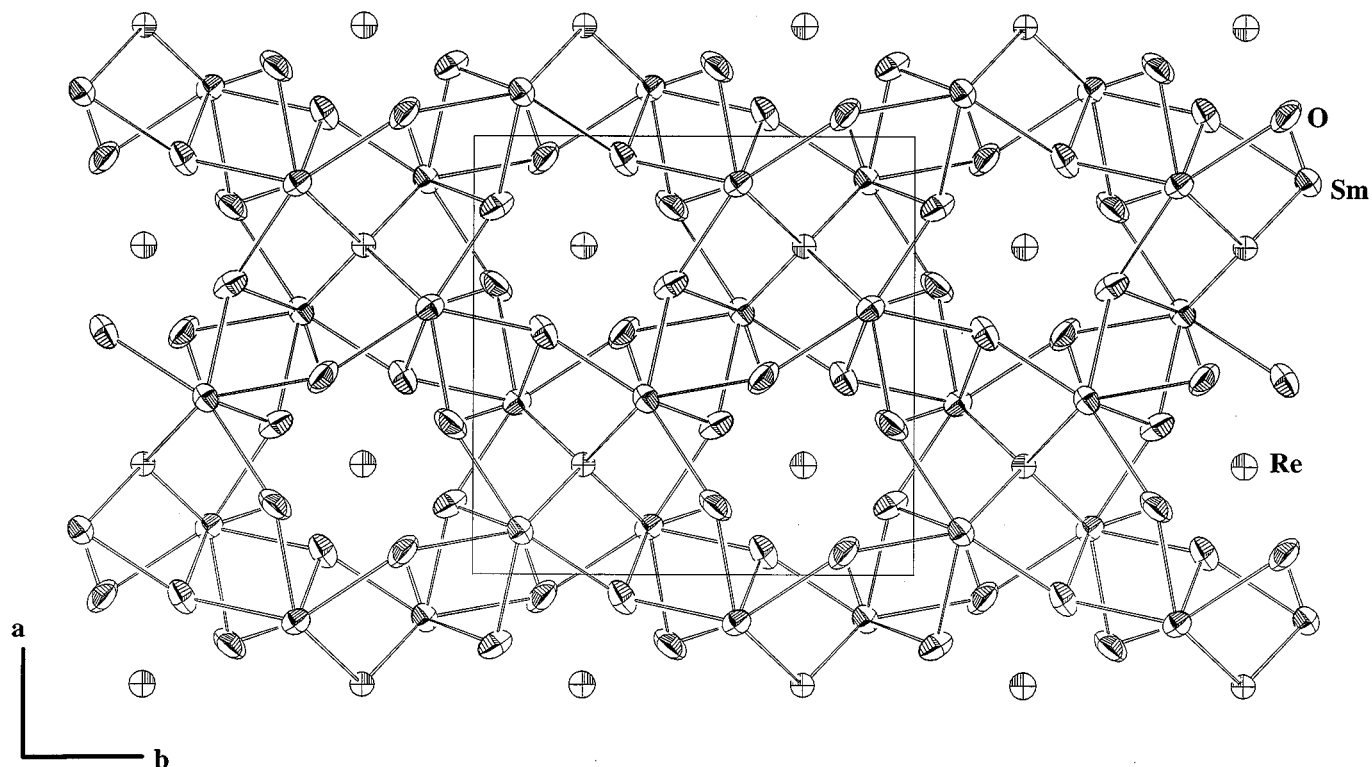

FIG. 1. Crystal structure of Sm_2ReO_5, viewed along the [001] direction including only samarium–oxygen bonds.
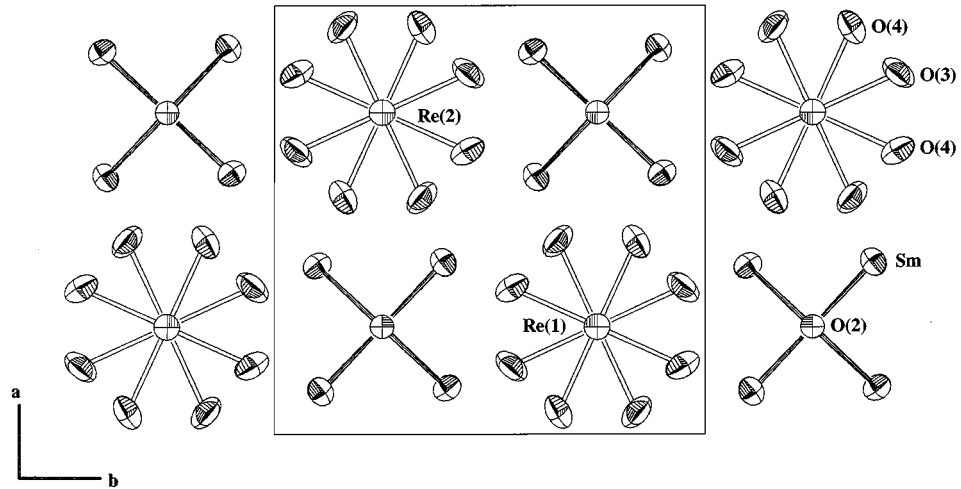
FIG. 2. Crystal structure of Sm$_2$ReO$_5$, viewed along the [001] direction including only rhenium–oxygen bonds and the bonds in Sm$_4$O tehtrahedra.
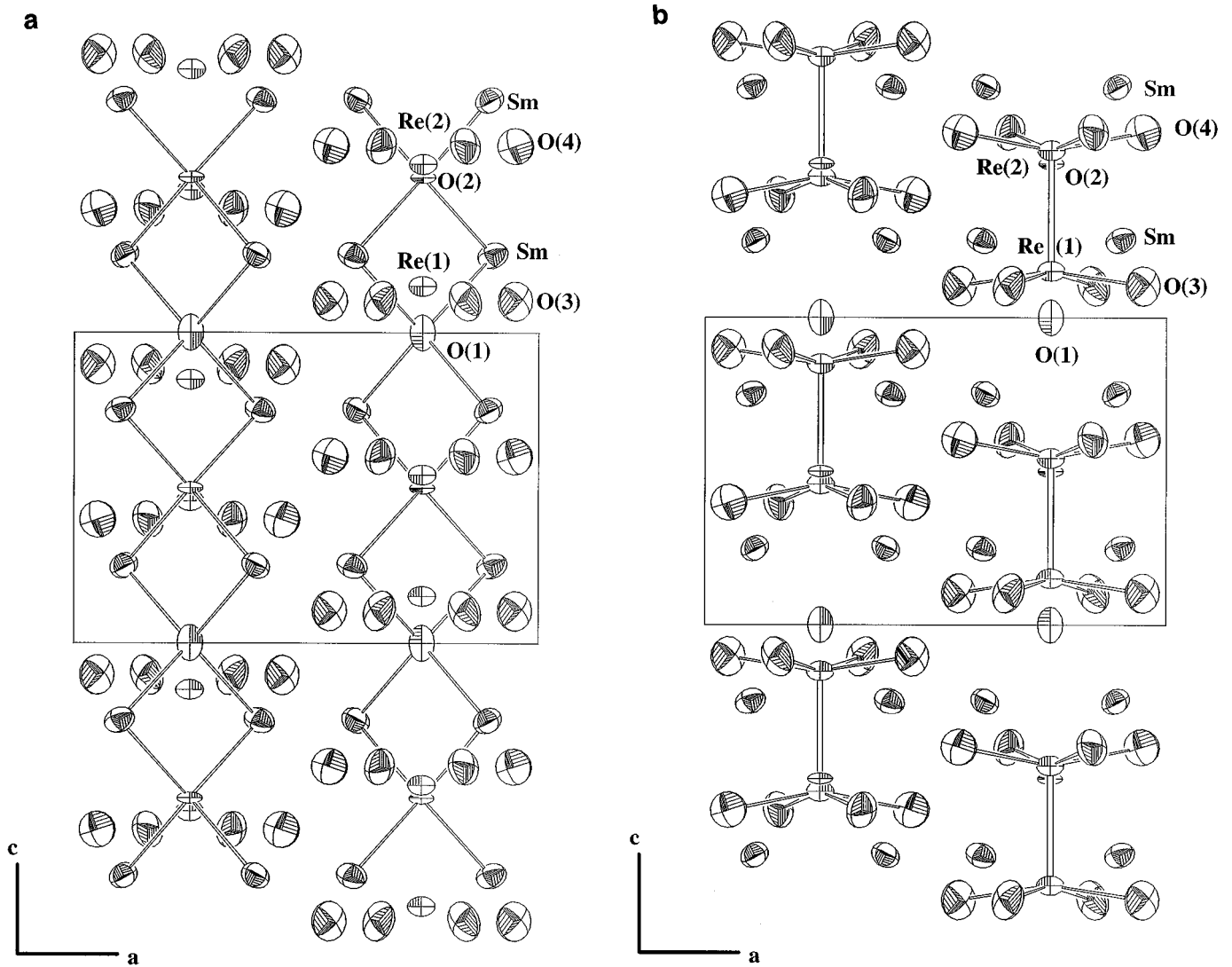

FIG. 3. Crystal structure of Sm$_2$ReO$_5$, viewed along the [010] direction. (a) Re$_2$O$_8$ units, and (b) corner-sharing Sm$_4$O tetrahedra, forming parallel [001] chains.

TABLE 4
Geometry Within Both "Quadratic" Layers in the Samarium Coordination and the Corresponding Plane Equations

(a) $2.198(0.019)x + 1.695(0.015)y + 5.443(0.005)z = 4.671(0.014)$		(b) $1.712(0.016)x + 2.230(0.021)y + 5.435(0.006)z = 1.969(0.018)$	
Atom	Deviation (Å)	Atom	Deviation (Å)
O(2)	−0.128(0.001)	O(1)	0.132(0.002)
O(4)	0.114(0.001)	O(3)	−0.137(0.001)
O(4a)	−0.119(0.001)	O(3b)	−0.118(0.002)
O(4c)	0.134(0.001)	O(3d)	0.123(0.002)
Sm(1)	−1.402(0.001)	Sm(1)	1.429(0.001)
Pair	Distance (Å)	Pair	Distance (Å)
O(2)–O(4)	2.787(5)	O(1)–O(3)	2.783(6)
O(4)–O(4a)	3.126(11)	O(3)–O(3d)	2.683(8)
O(4a)–O(4c)	2.665(8)	O(3d)–O(3b)	3.105(12)
O(4c)–O(2)	2.787(5)	O(3b)–O(1)	2.783(6)
Corner	Angle (°)	Corner	Angle (°)
O(2)–O(4)–O(4a)	84.30(23)	O(1)–O(3)–O(3d)	93.15(26)
O(4)–O(4a)–O(4c)	87.75(31)	O(3)–O(3d)–O(3b)	87.78(33)
O(4a)–O(4c)–O(2)	93.63(24)	O(3d)–O(3b)–O(1)	84.60(23)
O(4c)–O(2)–O(4)	92.53(5)	O(3b)–O(1)–O(3)	92.59(5)

Note. The symmetry operations are defined in the endnote of Table 3.

Antiferromagnetic ordering is deduced from the pronounced maximum in magnetization at 2.4(1) K. The large temperature-independent contribution arises from the Van Vleck paramagnetism of Sm(3+). If this contribution is attributed only to the Sm(3+) ions, a constant magnetization of $8.65 \times 10^{-4} \mu_B$ is derived for each Sm(3+) ion. With the assumption that the temperature dependence of magnetization is only due to the rhenium ions, an effective magnetic moment of 0.64 μ_B is derived from the Curie constant for each Re(4+) ion. Although the subdivision of samarium and rhenium contributions to the observed magnetization is rather arbitrary, the derived small value for the rhenium moment is an upper limit and gives a strong indication for a metallic character of the bond within the rhenium–rhenium pairs, because the expected value for an isolated Re(4+) ion is much larger, even a spin-only value
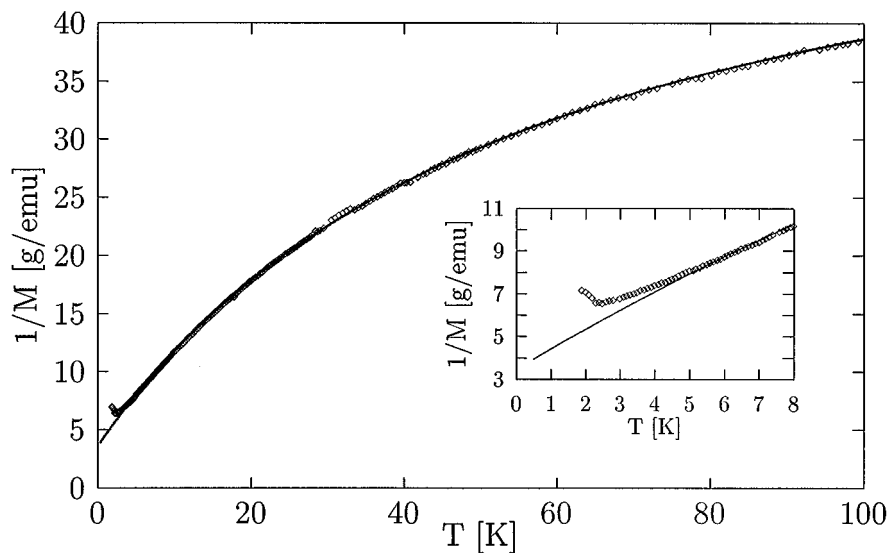

FIG. 4. Inverse magnetization of Sm_2ReO_5.

in the case of a low spin configuration (1.73 μ_B). To the author's knowledge, Sm_2ReO_5 is the first example of a compound with rhenium in the oxidation state $+4$, for which magnetic ordering is reported. However, it cannot be excluded that the observed maximum in the temperature dependence of magnetization is only due to the magnetic ordering of the samarium sublattice alone.

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