High Temperature Magnetic Susceptibility of Light Rare-Earth Tungstates

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This paper reports our results on the magnetic suscep-
tibility (χ_m) of light rare-earth (viz. Ce, Pr, Nd, Sm, Eu
and Gd) tungstates in the temperature range of 300 to
900 K. As expected the variation of χ_m with temperature
obeys the Curie-Weiss law ($\chi_m = C/T - \theta$). The values of
the Curie-constant (C), paramagnetic Curie temperature (θ)
and magneton number (p) for the magnetic ions of these
tungstates have been evaluated. The experimental p values
are in good agreement with the theoretical values of p for
these ions. Thus it is concluded that the magnetic ($4f$)
electrons remain intact with the respective ions at high
temperature and their participation in electrical conduction
is improbable. Negative values of θ normally indicate anti-
ferromagnetic ordering in these compounds at low tem-
peratures; however in these tungstates the crystal field
seems to be the prime reason for Curie-Weiss law behaviour
and negative values of θ. The magnetic behaviour of light
rare-earth tungstates in briefly discussed.

1. Introduction

Rare-earth compounds have become very inter-
esting from theoretical and experimental points of
view. Many of the rare-earth compounds are useful
in permanent magnet and laser materials, optical
filters, microwave computers and space technology
[1—4]. We have been studying the electrical and
magnetic properties of rare-earth sesquioxides [5, 6],
tungstates [7—12] and molybdates [13] for the last
six years. This paper reports on our study regarding
the molar magnetic susceptibility (χ_m) of light
rare-earth (viz. Ce, Pr, Nd, Sm, Eu and Gd)
tungstates in the temperature range of 300 to
900 K. At room temperature these tungstates have
monoclinic lattice structure [14] and belong to
space group F_2/d. All of them are fine grained
powders with typical colours. To the best of our
knowledge the magnetic properties of these com-
pounds have not been studied by other workers.

2. Materials and Experimental Techniques

These tungstates with a stated purity of 99.9%
have been procured from Rare-Earth Products

Limited, England. They have been used as such in
our study.

The magnetic susceptibility (χ_m) at high tem-
peratures ($T > 300$ K) of these powdered samples
was measured using Faraday's method employing
a sensitive magnetic balance (10^{-5} g) and electro-
magnets of typical pole pieces. The procedural
details are described elsewhere [15]. The accuracy
of the χ_m values at high temperatures is $\sim 3\%$
whereas at low temperatures it is $< 2\%$.

3. Results and Discussion

The variation of χ_m^{-1} of light rare-earth tungstates
with temperatures is shown in Figure 1. The curves
for all the samples are good straight lines, suggest-
ing Curie-Weiss law behaviour ($\chi_m = C/T - \theta$) and
a possible magnetic ordering at low temperatures
[16]. From the extrapolation of these straight lines
and their slopes one can obtain values of the
paramagnetic Curie temperature (θ) and Curie-
constant (C). From the value of C the effective
Bohr magneton (p) for the magnetic ions has been
calculated. The calculated values of these param-
eters are given in Table 1.

In these tungstates only rare-earth ions are
magnetic in nature and are presumed to exist in
trivalent states. From the ground state L, S and
J values of these ions one can evaluate [17] the free
ion theoretical values of p. These values are also
given in Table 1 for all the light rare-earth tung-
states. There is good agreement between the free
ion theoretical and experimental values of p
except for the Sm and Eu tungstates. However
Van Vleck and Frank [17] have reported the
effective p values for these magnetic ions, which are
in agreement with our experimental values. This
agreement indicates that the 4f electrons are intact
on their respective ions and thus their participation
in electrical conduction is least probable.

It is clear from Table 1 that the light rare-earth
tungstates have negative value of θ, which indicates
possible antiferromagnetic ordering at low tem-
peratures [16]. The insulating nature of these
compounds ($\sigma \sim 10^{-10}$ ohm^{-1} cm^{-1} at room tem-
perature) [15] rules out any direct exchange inter-
action between the rare-earth ions. Also it has been
shown by various workers [16, 18] that other types
of exchange interaction are very weak between the
rare-earth ions. Dipole interactions are also
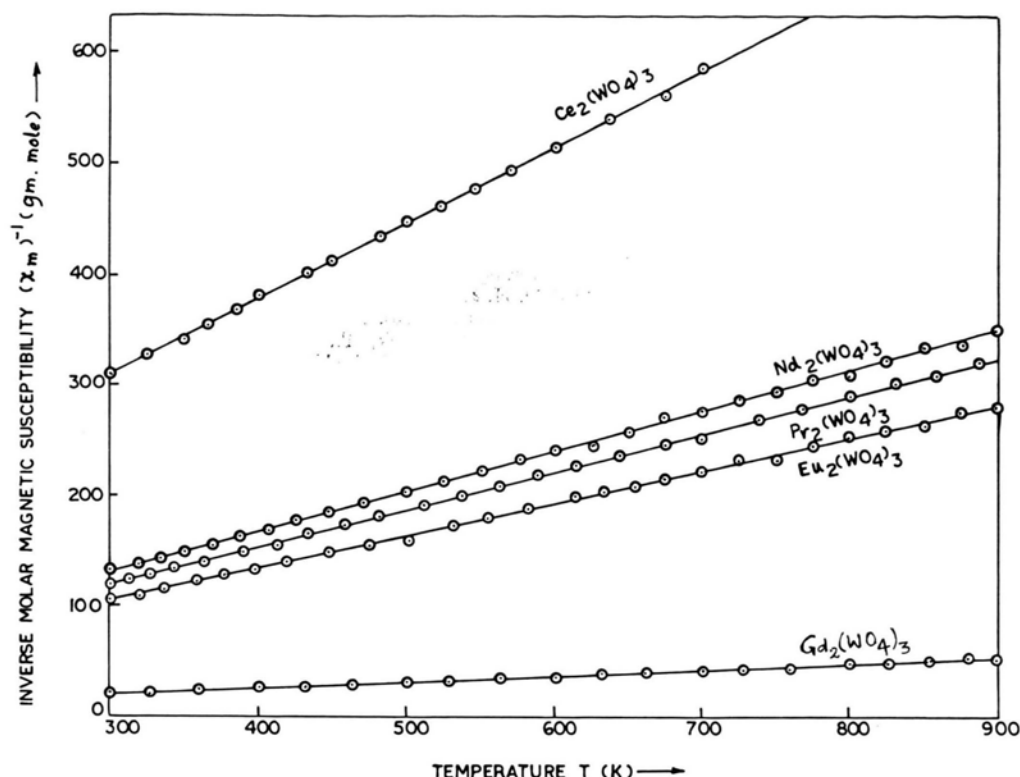expected to be very weak in view of the large

Fig. 1. Variation of inverse molar magnetic susceptibility $(\varkappa_m)^{-1}$ of light rare-earth tungslates from 300 to 900 k.

separation between these ions. Thus this negative value of θ is not expected due to magnetic ordering. The χ_m of $Sm_2(WO_4)_3$ is very weak at 300 K and we could not measure it accurately. However, our low temperature magnetic susceptibility results [8] too speak against exchange interaction and anti-ferromagnetic ordering, otherwise the inverse molar susceptibility of this compound ought to have risen and not fallen with decreasing tempera-ture. In view of these facts it can be said that the finite value of θ is dominantly caused by crystal

field interactions and not by superexchange or double exchange interactions. This is clearly seen in $Gd_2(WO_4)_3$. This compound has the magnetic ion Gd^{3+} which is spherically symmetric being in the orbital S state. Thus it has very small crystal field interaction giving $\theta = 0$ only if other inter-actions are negligible.

Acknowledgement

Table 1. Calculated values of different parameters and experimental p values.

Tungstates	Magnetic ion	Ground state	Molar Curie-constant Cm (K/emu-mole)	Paramagnetic Curie-temperature θ(K)	Effective Bohr magneton p		
					Theoretical free ion	Van-Vleck and Frank	Experi-mental
$Ce_2(WO_4)_3$	Ce^{3+}	$^2F_{5/2}$	1.50 ± 0.15	-160 ± 5	2.53	2.56	2.45 ± 0.10
$Pr_2(WO_4)_3$	Pr^{3+}	$^3H_4$	3.06 ± 0.15	$- 65 \pm 5$	3.58	3.62	3.50 ± 0.10
$Nd_2(WO_4)_3$	Nd^{3+}	$^4I_{9/2}$	3.10 ± 0.15	$- 60 \pm 5$	3.62	3.68	3.54 ± 0.10
$Sm_2(WO_4)_3$	Sm^{3+}	$^6H_{5/2}$	0.70 ± 0.20	$- 30 \pm 5$	0.84	1.60	1.65 ± 0.13
$Eu_2(WO_4)_3$	Eu^{3+}	$^7F_0$	2.95 ± 0.15	$- 40 \pm 5$	0.00	3.50	3.44 ± 0.10
$Gd_2(WO_4)_3$	Gd^{3+}	$^8S_{7/2}$	15.80 ± 0.10	0.0 ± 1	7.94	7.94	7.95 ± 0.06

[1] S. Methfessel and D. C. Mattice, Handbuch der Physik XVII/1, Ed. S. Flugges, Springer-Verlag Heidelberg, 1960, p. 389.
[2] K. N. R. Taylor, Contemp. Phys. 11, 423 (1970) and Adv. Phys. 20, 551 (1971).
[3] F. H. Spedding, Fifteenth edition of Encyclopedia Britannica. Inc. Printed in USA, Helen Hemingway Publisher 1974, p. 515.
[4] H. W. Katz, Solid State Magnetic and Dielectric Devices, John Wiley, New York 1959.
[5] N. Dar and H. B. Lal, Ind. J. Pure Appl. Phys. 14, 788 (1976).
[6] H. B. Lal, B. K. Verma, and N. Dar, Ind. J. Cryogenics 1, 119 (1976).
[7] H. B. Lal, N. Dar, and A. Kumar, J. Phys. C 7, 4335 (1974) and 8, 2745 (1975).
[8] H. B. Lal and N. Dar, Z. Naturforsch. 30a, 1783 (1975).
[9] H. B. Lal and N. Dar, Physica 84 B, 254 (1976).

[10] H. B. Lal and N. Dar, J. Phys. Chem. Solids 38, 161 (1977).
[11] H. B. Lal, N. Dar, and L. Lundgren, J. Phys. Soc. Japan 41, 1216 (1976).
[12] N. Dar and H. B. Lal, Pramana 11, 705 (1978).
[13] H. B. Lal and R. N. Pandey, Z. Naturforsch. 33a, 235 (1978).
[14] K. Nassau, H. J. Levinstein, and G. M. Loiacono, J. Phys. Chem. Solids 26, 1805 (1965).
[15] N. Dar, Electrical Transport and Magnetic Properties of some Rare-Earth compounds, Ph. D. Thesis, University of Gorakhpur, Gorakhpur 1976.
[16] D. H. Martin, Magnetism in Solids, Illeffe Book Ltd., London 1967, p. 201.
[17] J. H. Van Vleck, Theory of Electric and Magnetic Susceptibility, Oxford University Press, London 1932, p. 226.
[18] J. H. Thomas and M. J. Seinko, J. Chem. Phys. 61, 3920 (1974).