

High Temperature Magnetic Susceptibility of Light Rare-Earth Tungstates

Naseeb Dar and H. B. Lal

Department of Physics, University of Gorakhpur, India

Z. Naturforsch. **34a**, 892–894 (1979);
received April 30, 1979

This paper reports our results on the 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. 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 antiferromagnetic ordering in these compounds at low temperatures; 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 is briefly discussed.

1. Introduction

Rare-earth compounds have become very interesting 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 compounds 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 temperatures ($T > 300$ K) of these powdered samples was measured using Faraday's method employing a sensitive magnetic balance (10^{-5} g) and electromagnets 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, suggesting 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 parameters 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 tungstates. 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 temperatures [16]. The insulating nature of these compounds ($\sigma \sim 10^{-10}$ ohm $^{-1}$ cm $^{-1}$ at room temperature) [15] rules out any direct exchange interaction 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

Reprint requests to Dr. N. Dar, Department of Physics, University of Gorakhpur, Gorakhpur, Indien.

0340-4811/79/0700-0892 \$ 01.00/0



Dieses Werk wurde im Jahr 2013 vom Verlag Zeitschrift für Naturforschung in Zusammenarbeit mit der Max-Planck-Gesellschaft zur Förderung der Wissenschaften e.V. digitalisiert und unter folgender Lizenz veröffentlicht: Creative Commons Namensnennung-Keine Bearbeitung 3.0 Deutschland Lizenz.

Zum 01.01.2015 ist eine Anpassung der Lizenzbedingungen (Entfall der Creative Commons Lizenzbedingung „Keine Bearbeitung“) beabsichtigt, um eine Nachnutzung auch im Rahmen zukünftiger wissenschaftlicher Nutzungsformen zu ermöglichen.

This work has been digitalized and published in 2013 by Verlag Zeitschrift für Naturforschung in cooperation with the Max Planck Society for the Advancement of Science under a Creative Commons Attribution-NoDerivs 3.0 Germany License.

On 01.01.2015 it is planned to change the License Conditions (the removal of the Creative Commons License condition "no derivative works"). This is to allow reuse in the area of future scientific usage.

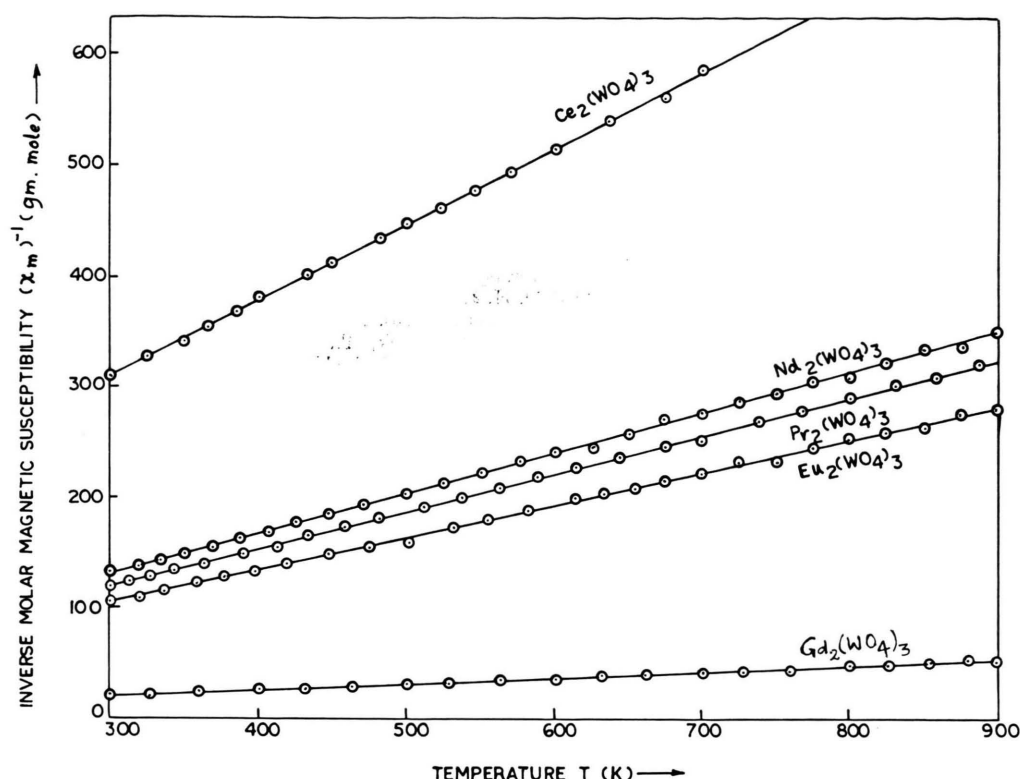


Fig. 1. Variation of inverse molar magnetic susceptibility $(\chi_m)^{-1}$ of light rare-earth tungstates from 300 to 900 K.

separation between these ions. Thus this negative value of θ is not expected due to magnetic ordering. The χ_m of $\text{Sm}_2(\text{WO}_4)_3$ 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 temperature. 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 $\text{Gd}_2(\text{WO}_4)_3$. 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 interactions are negligible.

Acknowledgement

One of us (N.D.) is grateful to CSIR (India) for a Post-Doctoral Fellowship.

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

Tungstates	Magnetic ion	Ground state	Molar Curie-constant C_m (K/emu-mole)	Paramagnetic Curie-temperature θ (K)	Effective Bohr magneton p		
					Theoretical free ion	Van-Vleck and Frank	Experimental
$\text{Ce}_2(\text{WO}_4)_3$	Ce^{3+}	$^2F_{5/2}$	1.50 ± 0.15	-160 ± 5	2.53	2.56	2.45 ± 0.10
$\text{Pr}_2(\text{WO}_4)_3$	Pr^{3+}	3H_4	3.06 ± 0.15	-65 ± 5	3.58	3.62	3.50 ± 0.10
$\text{Nd}_2(\text{WO}_4)_3$	Nd^{3+}	$^4I_{9/2}$	3.10 ± 0.15	-60 ± 5	3.62	3.68	3.54 ± 0.10
$\text{Sm}_2(\text{WO}_4)_3$	Sm^{3+}	$^6H_{5/2}$	0.70 ± 0.20	-30 ± 5	0.84	1.60	1.65 ± 0.13
$\text{Eu}_2(\text{WO}_4)_3$	Eu^{3+}	7F_0	2.95 ± 0.15	-40 ± 5	0.00	3.50	3.44 ± 0.10
$\text{Gd}_2(\text{WO}_4)_3$	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* **84B**, 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).