

Magnetic and transport properties of some light rare earth tungstates

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Abstract. Measurements relating to molar magnetic susceptibility, dc electrical conductivity and thermoelectric power of Nd, Sm, Eu and Gd are reported. The ac electrical conductivity at a few temperature ranges is also given. It is found that it follows the Curie-Weiss law behaviour and this has been attributed to the crystal field effect. The experimental value of Bohr magneton for the magnetic ions has been found to be in good agreement with theory. Thermoelectric power is negative in the measured temperature range suggesting these materials to be *p*-type semi-conductors and holes as the dominant charge carriers. The results are explained using band theory.

Keywords. Magnetic susceptibility; electrical conductivity; thermo-electric power; rare-earth tungstates.

1. Introduction

Rare-earth compounds have become sufficiently interesting due to their unique physical properties and potential promise in technology (Methfessel and Mattis 1968; Taylor 1970, 1971; Spedding 1974). We have been studying the transport and magnetic properties of rare-earth compounds (Lal *et al* 1974, 1975, 1976a, b); Lal and Dar 1975, 1976a, b, 1977; Dar and Lal 1976; Pratap and Verma 1978). This paper reports our study on the magnetic susceptibility (χ_m), electrical conductivity (a.c. and d.c.), and thermoelectric power (**H**) of some light rare-earth tungstates (LRET), which do not appear to have been studied earlier. Our prepared samples were in powdered form and pressed pellets for σ , **H** and measurements were used. Single crystals could not be prepared due to experimental limitations. At room temperature these tungstates have monoclinic lattice structure (Nassau *et al* 1965; Brixner and Sleight 1973) and belong to F_2/d space-group. The lattice parameters, melting point, density, etc. of these tungstates at room temperatures are given in table 1.

2. Sample preparation and experimental technique

Tungstates of the type $Ln_2(WO_4)_3$ (where $Ln = Nd, Sm, Eu$ and Gd) in powder form were prepared by the standard method reported by Brixner and Sleight (1973). The starting materials used were rare-earth sesquioxides (99.9% Rare-Earth Products, England) and analytical grade WO_3 (99.9%, E. Merck, Germany) both dried at 900K for a few hours. The range of melting points of the sample is given in table 1. Mass

Table 1. Lattice parameters, melting point and density, etc. of some light rare-earth tungstates*.

Tungstates	Lattice parameters				Melting point °C	Density d.g cm ⁻³	Volume Å ³
	a, Å	b, Å	c, Å	β°			
Nd ₂ (WO ₄) ₃	7.765	11.614	11.544	109.8	1135	7.04	979.55
Sm ₂ (WO ₄) ₃	7.711	11.504	11.468	109.8	1155	7.32	957.52
Eu ₂ (WO ₄) ₃	7.684	11.465	11.426	109.6	1165	7.37	948.35
Gd ₂ (WO ₄) ₃	7.670	11.411	11.321	109.6	1230	7.49	933.27

*Data are taken from Nassau *et al* (1965) and Brixner and Sleight (1973).

spectrographic studies were not made. The impurities (0.1%) expected were in the form of oxides or tungstates.

The magnetic susceptibility (χ_m) of these powdered samples at high temperature ($T > 300\text{K}$) was measured using Faraday's method employing a sensitive magnetic balance (10^{-5}g) and electromagnets of typical pole pieces. Procedural details are described elsewhere (Dar 1976). The accuracy of χ_m values at high temperature ($\sim 800\text{K}$) is $\pm 3\%$ whereas at low temperature it is less than 2%.

The measurements were made using powdered specimens pelletised at a pressure ranging from $2 \times 10^6 \text{ g cm}^{-2}$ to $10 \times 10^6 \text{ g cm}^{-2}$, as well as a hand operated hydraulic press and a suitable die. The pellets were annealed for a few hours at 1200 K, cleaned, dried and gently silver-painted on two faces before they were put into the sample holder. The sample holder for **H** measurement was specially designed (Lal *et al* 1976b) for this purpose. A thermal gradient ($\nabla T \sim 20\text{K}$) is produced across the sample with the help of a small heater placed just below one of the hard electrodes. The thermoelectro motive force (∇E) developed across the pellet was measured by a Keithley digital multimeter type 171 with an internal impedance of $10^{10}\Omega$. The temperature (∇T) was measured using chromel alumel thermocouples. The ratio ($\nabla E / \nabla T$) gives the value of **H** with an overall accuracy of 10%. For the measurement of σ , the two-electrode method was employed. Platinum foil and silver paint were used as electrode materials. The electrical conductivity (dc) of the pellets was measured using Keithley digital multimeter type 171. AC conductivity was measured at 1.542 kHz using a Weine-Kerr Bridge and at 100 Hz, 1 kHz and 10 kHz by LCR Bridge type 921. The procedural details are described in Dar (1976).

3. Results and discussion

The variation of inverse molar magnetic susceptibility (χ_m^{-1}) with temperature from 300 to 950 is shown in figure 1. The curves for all the samples show straight lines, suggesting a Curie-Weiss law behaviour ($\chi_m = C/T - \theta$) and a possible magnetic ordering at low temperature (Morrish 1966). From the extrapolation of these lines and their slopes one can obtain the values of paramagnetic Curie-temperature (θ), and Curie-constant (C). From C value, the effective number of Bohr magneton (p) for the magnetic ions has been calculated and is given in table 2.

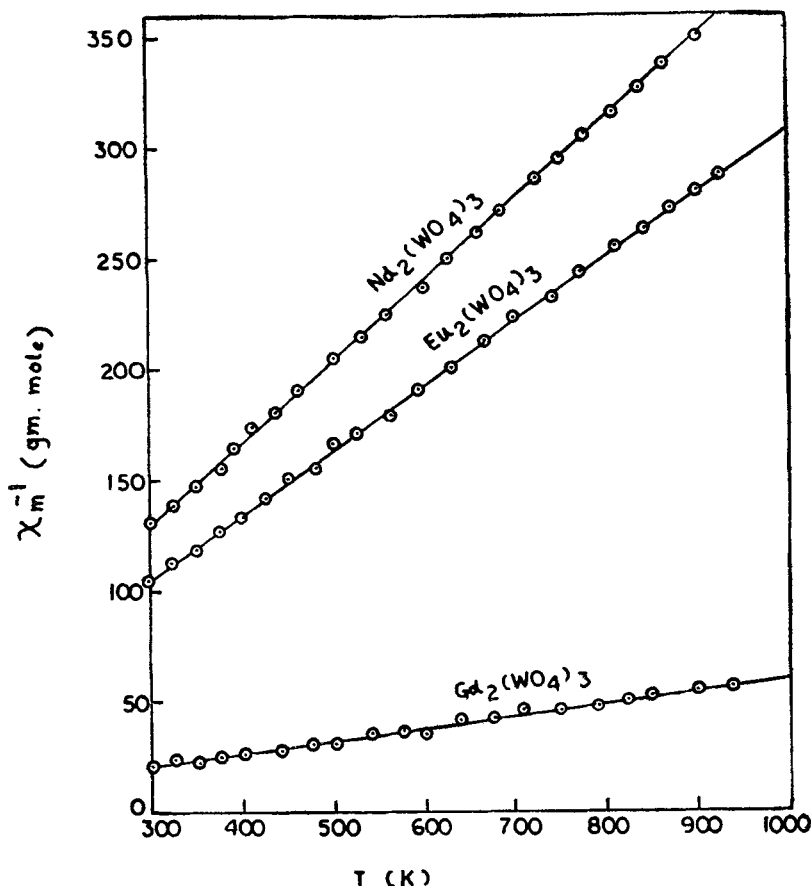


Figure 1. Variation of inverse molar magnetic susceptibility (χ_m^{-1}) with temperature (T) of some light rare-earth tungstates from 300 to 950 K.

Table 2. Calculated values of different parameters and experimental p values

Tungstates	Magnetic ion	C (K/emn-mole)	θ (K)	Effective Bohr magneton (p)		
				Theoretical free ion	Van Vleck and Frank	Experimental
Nd ₂ (WO ₄) ₃	Nd ³⁺	3.13	-60	3.62	3.68	3.49
Sm ₂ (WO ₄) ₃	Sm ³⁺	0.70	-30	0.84	1.60	1.65
Eu ₂ (WO ₄) ₃	Eu ³⁺	2.94	-40	0.00	3.50	3.40
Gd ₂ (WO ₄) ₃	Gd ³⁺	15.88	0	7.94	7.94	7.88

In these tungstates only rare-earth ions, which are magnetic in nature, are presumed to exist in trivalent states. From the ground state L , S and J values of these ions one can evaluate (Van-Vleck 1932) the free ion theoretical values of p (see table 2). There is a good agreement between theory and experiment.

It is seen from table 2 that the LRET have a negative θ value, indicating possible antiferromagnetic ordering at low temperatures (Morrish 1966). The insulating

nature of these compounds ($\sigma \sim 10^{-11}$ ohm $^{-1}$ cm $^{-1}$ at room temperature) rules out any direct exchange interaction between the rare-earth ions. It has also been shown by various workers (Martin 1967; Thomas and Seinko 1974) that other types of exchange interactions are very weak between the rare-earth ions. Dipole interactions are also expected to be very weak in view of the large separation between these ions. Therefore, the negative θ value is not expected to be due to magnetic ordering. Magnetic susceptibility of $\text{Sm}_2(\text{WO}_4)_3$ is very low above 300 K and accurate measurements could not be made. However, the low temperature magnetic susceptibility results earlier reported (Lal and Dar 1975) also point out against exchange interaction and antiferromagnetic ordering. Otherwise, the inverse susceptibility of this compound ought to have risen and not fallen with decreasing temperature. In view of these it can be said that the finite value of θ is mainly caused by crystal field interactions and not by superexchange or double exchange interactions. This is clearly seen in $\text{Gd}_2(\text{WO}_4)_3$, a compound that has a magnetic ion Gd^{3+} which is spherically symmetrical in orbital S state. It thus has a very small crystal field interaction giving $\theta=0$, only if the other interaction is negligible.

The density (d_p) and electrical conductivity (σ_p) of pellets annealed round 1200K for 20 hr increase almost linearly with pelletising pressure (P) upto $P \sim 3 \times 10^6$ g cm $^{-2}$. This increase becomes slow for high values of P and is almost constant for pellets made at $P > 6 \times 10^6$ g cm $^{-2}$. However the density of the pellets made at a high pressure ($P \sim 10 \times 10^6$ g cm $^{-2}$), remains slightly less than the reported x-ray density of the material. Thus, to account for the pore fraction ($f = (d_o - d_p)/d_o$), σ_p have been corrected. The crystalline value of σ has been obtained using the relation (Russel 1935),

$$\sigma = \sigma_p \left(1 + \frac{f}{1 + f^{2/3}} \right). \quad (1)$$

The H value does not significantly depend upon P and therefore no correction for pore fraction has been applied to it.

The σ values initially depend on heating and cooling cycles but after few heating and cooling cycles (3-4), they repeat in successive cycles. These repeatable values have been taken as the bulk value of the parameter for the solid. σ does not depend upon the electrode materials (silver paint, silver foil platinum foil, etc.) within the accuracy of our measurement. However platinum foil electrodes have been preferred for high temperature measurement. For platinum electrode dc I-V characteristics are linear upto the applied electric field of 0.1 kV/cm.

Figure 2 shows the variation of $\log \sigma$ dc with $10^3/T$ for the tungstates of Nd, Sm and Gd. It is seen that the curves are almost linear for Sm and Gd tungstates in the temperature range 650 to 1200K. A slight discrepancy is observed round 1020K to 1050K for $\text{Nd}_2(\text{WO}_4)_3$. A similar discrepancy is witnessed in ϵ' vs $T(K)$ curve for this substance at the same temperature indicating phase transition between 1020 to 1050K. However no significant change occurs in the slope of $\log \sigma_{dc}$ vs $10^3/T$ straight lines above and below this temperature. The results for $\text{Eu}_2(\text{WO}_4)_3$ have already been reported by us elsewhere (Lal *et al* 1976a). Figure 3 shows the variation of σ_{ac} of $\text{Gd}_2(\text{WO}_4)_3$ with frequency of applied ac signals at different temperatures (500 to 1000K). Similar curves are obtained for other tungstates. It is seen that the ac and

dc conductivities are almost the same for $T > 700\text{K}$ except that at lower temperature $\sigma_{dc} < \sigma_{ac}$. Figure 4 shows H variation with inverse of temperature from (800-1150K). H values are negative for all the samples indicating the dominance of positive charge carrier in these material. However the H values for all these solids do not vary much with temperature.

It is common to explain electrical transport in solids using band theory with appropriate scattering mechanism. In most of the rare-earth solids $5d$ cation band is regarded as the conduction band which however splits into t_{2g} and eg sub-bands by crystal fields. These bands are usually narrow ($\sim 1\text{ eV}$) in most of the rare-earth solids (Adler 1968 and Methfessel-Mattis 1968). The susceptibility data of these materials are compatible with $Ln : 4f$ core upto 900K. This indicates that $4f$ electron of the cation are localised and the probability for their participation in electrical conduction is ruled out. This gives $O^{2-} : 2p$ band as the other appropriate band for

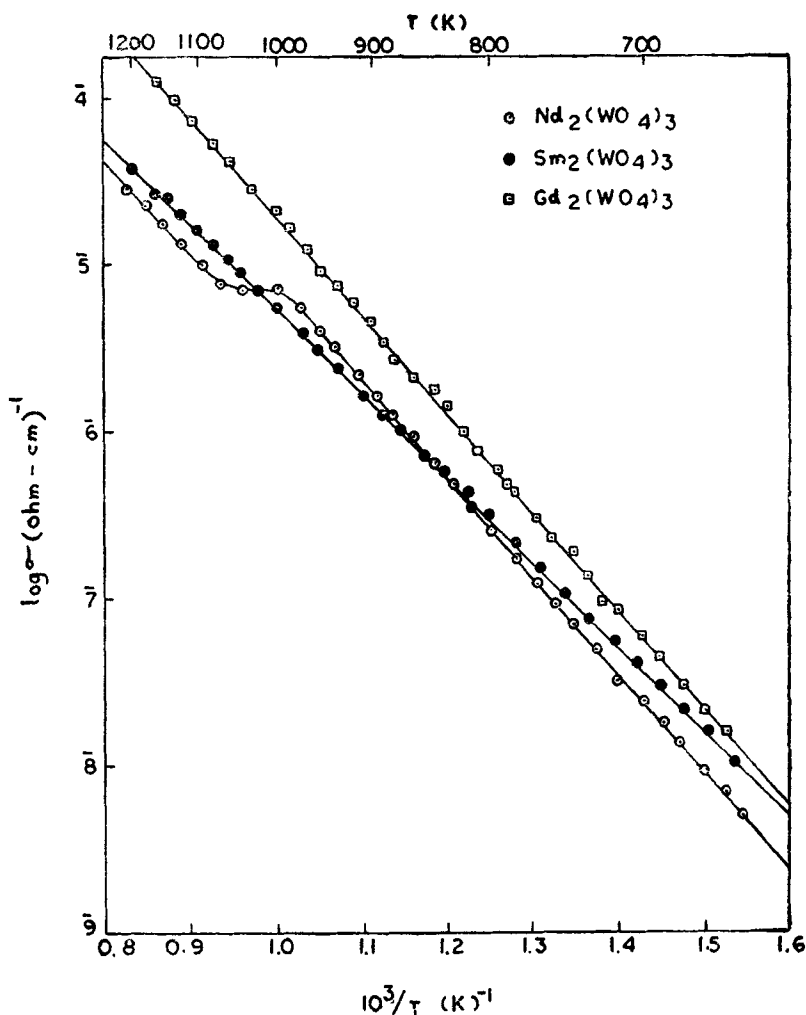


Figure 2. Variation of $\log \sigma$ vs $10^3/T (K)^{-1}$ for some light rare-earth tungstates from 625 to 1200 k.

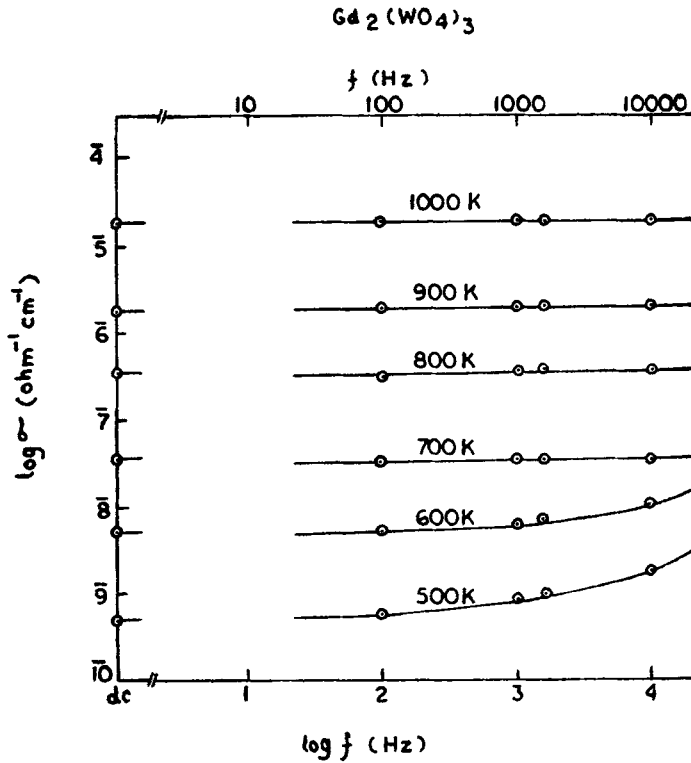


Figure 3. Variation of $\log \sigma$ with $\log f$ of $Gd_2(WO_4)_3$ at constant temperature (500 to 1000K).

electrical conduction and can be regarded as the valence band in these solids. $O^{2-}:2p$ is a normal wide band as compared to split $5d$ band. Thus the mobility of holes (μ_h) is expected to be large as against that of electrons (μ_e). On a two band model all tungstates should be of p -type intrinsic semiconductors and conductivity can be expressed by the relation,

$$\sigma = 2e (2\pi kT/h^2)^{3/2} (m_e m_h)^{3/4} (\mu_e + \mu_h) \exp(-E_g/2kT), \quad (2)$$

$$= \sigma_0(T) \exp(-E_g/2kT), \quad (3)$$

$$\sigma_0(T) = 2e (2\pi kT/h^2)^{3/2} (m_e m_h)^{3/4} (\mu_e + \mu_h), \quad (4)$$

$$= K' T^{3/2} a^{3/4} (1 + C) m_h^{3/2} \mu_h, \quad (5)$$

and $K' = 2e (2\pi k/h^2)^{3/2}$, $a = (m_e/m_h)$, $C = (\mu_e/\mu_h)$,

where k and h are Boltzman and Plancks constant, m_e and m_h are effective masses of the electron in conduction band and hole in valence band respectively, μ_e and μ_h are the mobilities of the electron and the hole and E_g is the energy band gap of the solid. The variation of $\sigma_0(T)$ with temperature is negligibly small in comparison to exponential term in (2). Hence the plot of $\log \sigma$ vs $1/T$ curve should be straight line for

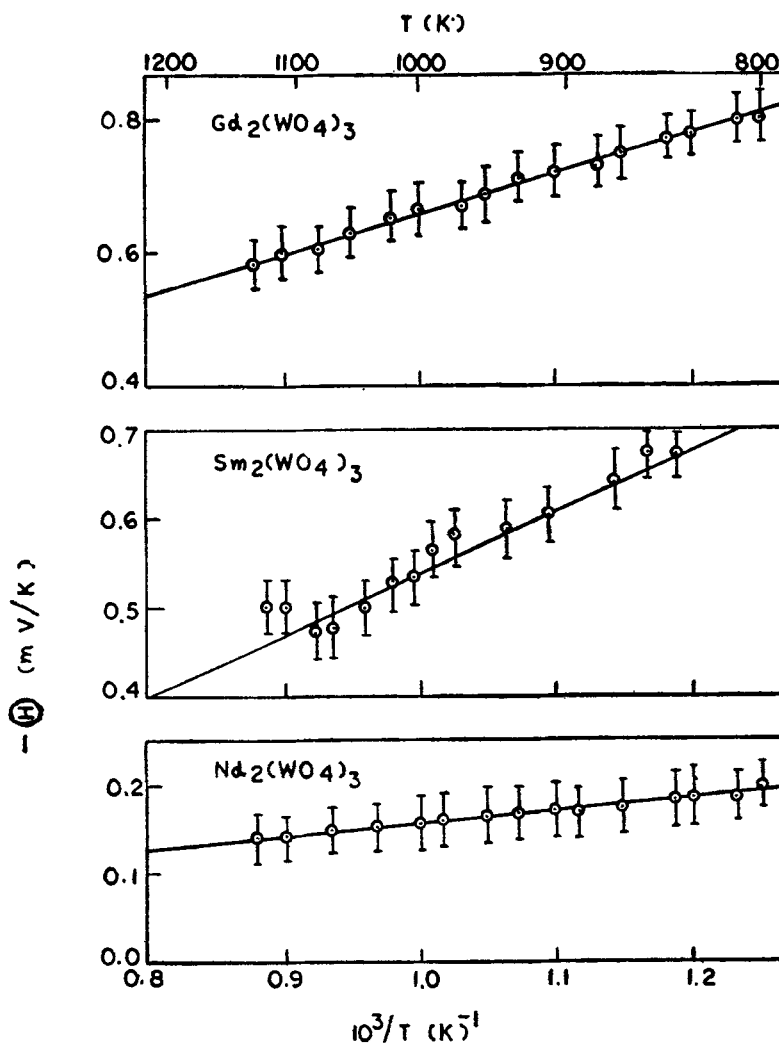


Figure 4. Variation of thermoelectric power H vs $10^3/T$ (K) $^{-1}$ for some light rare-earth tungstates from 800 to 1150K.

intrinsic semiconductors. The plot of $\log \sigma$ vs $10^3/T$ are actually straight line in the temperature range 650 to 1200K for Sm and Gd tungstates. The curve for $Nd_2(WO_4)_3$ is also straight line above and below phase transition temperature. From these straight lines one can evaluate $\sigma_0(T)$ and E_g for these materials. The evaluated values for these parameters are given in table 3. E_g values are ~ 2 eV and seem quite reasonable.

Two band model in the simplest approach yield following relation for the variation of H with temperature (Herman and Honing 1976).

$$H = \left[\frac{E_g(C-1)}{2e(C+1)} \right] \frac{1}{T} + \frac{2k(C-1)}{e(C+1)} + \frac{3k}{4e} \log_e(a), \quad (6)$$

$$= \frac{\eta}{T} + K, \quad (7)$$

Table 3. Some transport parameters for some light rare-earth tungstates

Tungstates	E_g (eV)	$\sigma_0(T)$ (cm^{-1})	η (mV)	K (mV)	$C(\mu_e/\mu_h)$	$a = m_e/m_h$	$\frac{\mu_h}{\text{cm}^2/\text{V sec.}}$
$\text{Nd}_2(\text{WO}_4)_3$	2.60	69.9	-0.15	± 0.005	0.767	1.43 ± 0.11	$1.29 - 1.06^a$
	2.50	26.0	-0.15	± 0.005	0.786	1.38 ± 0.11	$1.06 - 0.53^b$
$\text{Sm}_2(\text{WO}_4)_3$	2.00	0.65	-0.60	+ 0.060	0.25	6.76	$(1.15 - 0.43) 10^{-2c}$
	1.86*						
$\text{Gd}_2(\text{WO}_4)_3$	2.36	18.24	-0.65	± 0.01	0.290	4.4 ± 0.7	$0.43 - 0.16^c$

a — higher value at 1050K and lower value at 1200K; b — higher value at 625 and lower value at 1000K; c — higher value at 625 and lower value at 1200K.

*value if intermediate polaron dominate in electrical conduction.

$$\text{with } \eta = \frac{E_g (C - 1)}{2e (C + 1)}, \quad (8)$$

$$K = \frac{2k(C - 1)}{e(C + 1)} + \frac{3}{4} \frac{k}{e} \log_e (a). \quad (9)$$

It is important to point out that we have changed sign in the original relation of the authors because we have used the internationally accepted relation $\mathbf{H} = \nabla E / \nabla T$. In this relation, the thermoelectric power has a typical sign opposite to that of charge carriers of the mobile species. However, Pratap and Verma (1978) have used the conventional relation of Herman and Honing (1976) with $C=0$. In band conduction it is reasonable to assume that both C and (a) will be fairly constant with temperature. Thus a plot of \mathbf{H} vs $10^3/T$ should also yield a straight line. The experimental \mathbf{H} vs $1/T$ curves are actually good straight lines and give good support to the above model for these solids. From these values of η , K and the known value of E_g from the electrical conductivity results, it is easy to evaluate C and a and these values are given in table 3. From the known values of C , a and $\sigma_o(T)$ one can also evaluate the value of μ_e and μ_h in terms of m_h using (5). The exact values of m_h are not known for any of these solids. However, one can estimate the value of μ_e and μ_h by taking $m_h=m$ (the free electron mass). The computed values of μ_h for all these tungstates are given in table 3. It is seen from this table that for $\text{Nd}_2(\text{WO}_4)_3$ and $\text{Gd}_2(\text{WO}_4)_3$ the mobility values are quite large viz ~ 1 to $0.1 \text{ cm}^2/\text{V sec}$ and appropriate for normal band conduction. Thus one can say that the electrical conduction in $\text{Nd}_2(\text{WO}_4)_3$ and $\text{Gd}_2(\text{WO}_4)_3$ takes place via band mechanism.

In the case of $\text{Sm}_2(\text{WO}_4)_3$ the mobility values are $\sim 2 \times 10^{-3}/\text{V sec}$ at 625K and $\sim 4 \times 10^{-3} \text{ cm}^2/\text{V sec}$ at 1200K (table 3). These are too small to strengthen the concept of band conduction. In view of such low mobilities of charge carriers, ionic nature and high dielectric constant value of the material, one should expect formation of polarons in this compound. It is therefore reasonable to discuss our results for this material from a polaronic concept which is well developed and reviewed by several authors (Appel 1968, Austin and Mott 1969, Bosman and Van Dall 1970): One of the important parameters of polaron is the dimensionless coupling constant (α) given by the expression

$$\alpha = \frac{e^2}{\epsilon_p} (m^*/2\hbar^3 \omega_0)^{1/2}, \quad (10)$$

$$\text{and } \epsilon_p = \frac{\epsilon_0 \epsilon_\infty}{\epsilon_0 - \epsilon_\infty}, \quad (11)$$

where \hbar is the rationalised Planck's constant, e is electronic charge, m^* is the rigid lattice effective mass of the charge carrier, ϵ_0 and ϵ_∞ are the static and optical dielectric constants of the material and ω_0 is the infrared optical mode frequency. None of these parameters is accurately known for this solid. However, for a rough estimate of α , one can take $\omega_0 \sim 10^{14} \text{ Hz}$ (values reported for isostructural solids) and a value of $\epsilon_0 = 16.45 \pm 0.5$ and $\epsilon_\infty^\dagger \sim 4.00$. Taking $m^*=m$, one gets $\epsilon_p = 5.28$ and $\alpha = 1.99$. This

[†] ϵ_∞ values have been evaluated by the extrapolation of the curve between the real part of the dielectric constant and frequency to 10^{19} Hz .

value is suitable for intermediate polarons (Bosman and Van Dall 1970). The mobility of intermediate polaron is given by the relation

$$\mu = \mu_0 \exp - (\hbar\omega_0/kT), \quad (12)$$

and if the intermediate polarons are produced by thermally generated intrinsic charge carriers then the electrical conductivity takes the form

$$\sigma = \sigma_0 (T) \exp - (E_g + 2\hbar\omega_0/2kT). \quad (13)$$

The thermoelectric power in such a case has a slight negative slope as observed for $\text{Sm}_2(\text{WO}_4)_3$ (Sumi 1972). Analysing our data in terms of intermediate polaron yields $E_g=1.86$ eV against 2.00 eV. The mobility values will not be different to those given in table 3. It is worth pointing out that we have earlier observed intermediate polarons as the dominant charge carrier in $\text{Eu}_2(\text{WO}_4)_3$ (Lal *et al* 1976a). Thus the conduction mechanism and the magnetic behaviour of Eu and Sm tungstates differ from other tungstates.

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