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Electrical transport properties of $CuWO_4$

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Abstract. The temperature dependence of the electrical conductivity, thermoelectric power and dielectric constant of the antiferromagnetic $CuWO_4$ have been studied in the temperature range 300–1000 K. The conductivity results can be summarised by the equations $\sigma_I = 6{\cdot}31 \times 10^{-3} \exp(-0{\cdot}29\ \text{eV/kT})\ \text{ohm}^{-1}\ \text{cm}^{-1}$ in the temperature range 300-600 K and $\sigma_{II} = 3{\cdot}16 \times 10^{5} \exp(-1{\cdot}48\ \text{eV/kT})\ \text{ohm}^{-1}\ \text{cm}^{-1}$ between 600 K and 1000 K. The thermoelectric power can be expressed by $\theta = [-1{\cdot}25\ (10^3/T) + 3{\cdot}9]$ mV/K. Initially dielectric constant increases slowly but for high temperatures its increase is fast.

Keywords. Electrical conductivity; thermoelectric power; dielectric constant; copper tungstate.

1. Introduction

The study of the metal tungstates is of considerable importance from fundamental as well as industrial point of view (Li and Wang 1956; Rastogi *et al* 1978). The magnetic properties of transition metal tungstates with the general formula MWO_4 (where M=Cu, Mn, Fe, Co and Ni, etc.) has been studied in a wide temperature range (Anderes 1972; Cimpal and Kosek 1967; van Uitert *et al* 1964; Shapovalova *et al* 1967). But the transport properties of these materials have yet not been investigated. $CuWO_4$ is one of the prime members of the transition metal tungstate (TMT) family. It is an antiferromagnetic compound with Neel temperature 24 K (Anderes 1972). The ideal Wolframite structure of $CuWO_4$ is triclinic (Gebert and Kihlborg 1967) the space group is $P\bar{1}$ (Anderes *et al* 1973), with unit cell dimensions $a = 4{\cdot}70$Å, $b = 5{\cdot}84$Å, $c = 4{\cdot}88$Å, and $\alpha = 91{\cdot}7°$, $\beta = 92{\cdot}4°$, $\gamma = 82{\cdot}8°$. The magnetic unit cells, determined by neutron diffraction (Weitzel 1973) (2 *a*, *b*, *c*) are twice the chemical unit (*a*, *b*, *c*). The Shubnikov group is P_a (2/*c*). In the present paper we analyse and report the transport properties viz. a.c. electrical conductivity σ, thermoelectric power θ and dielectric constant ϵ' above room temperature (300-1000 K).

2. Experimental details

$CuWO_4$ in powder form (purity 99·9%) was procured from Ventron Corporation, USA and used as such. For σ, θ, and ϵ' measurements, powder samples were pelletised at the pressure $7{\cdot}69 \times 10^6$ g/cm² in pellet form using a hydraulic press and a suitable die. The pellet was pressed between platinum electrodes mounted on a stainless steel sample holder. A mica sheet was used for insulation. Details of the

sample holder assembly are similar to that of Shahi and Chandra (1975). Before the measurements, the pellet was silver painted on both the surfaces for better contact with the platinum electrodes and annealed for nearly 36 hr at 800 K. σ was measured using conductivity meter (Systronics type 302') which works at 50 Hz in 0·1–10μ mhos range and at 2 kHz in higher ranges with an accuracy better than 3%. The thermo e.m.f. (ΔV) developed across the pellet was measured with a vernier potentiometer. A temperature difference ($\Delta T = 20 \pm 2$K) was produced across the pellet with a microheater placed just below one of the electrodes. Temperatures were measured using chromel-alumel thermocouples. The ambient temperature was taken to be the mean of the temperatures at both ends. The overall accuracy in θ measurement was nearly 10%. The dielectric constant of the pellet was determined by measuring the capacity of the condenser formed by two electrodes using pellet as dielectric at 1 kHz using a Ruttonsha Simpson Universal Bridge model 901-I whose accuracy of measurement was $\pm$ 1·25% of reading $\pm$ 0·25% of range full scale.

3. Results and discussion

The electrical conductivity (σ) and dielectric constant (ϵ') both depend upon pelletising pressure. Both increase linearly with pelletising pressure and become almost constant above $P > 6 \times 10^6$ g cm^{-2}. But the measured density of the highest pressed pellet was only 80% of the reported density of $CuWO_4$ determined by x-ray. The crystalline value of σ and ϵ' is given by the relation (Russel 1935) taking account of pore fraction

$$\sigma(C) = \sigma(P)\,[1 + f/(1 + f^{2/3})], \tag{1}$$

$$\epsilon'(C) = \epsilon'(P)\,[1 + f/(1 + f^{2/3})], \tag{2}$$

where $f = (d_0 - d_p)/d_0$ is the volume pore fraction of the pellet. These formulae have modified the measured values of σ and ϵ' by about 20%.

The electrical conductivity as a function of temperature is shown in figure 1. It is seen that plots of log σ vs $10^3/T$ are linear in the temperature ranges 300-600 K and 600-1000 K with different activation energies. The results can be summarised by the following equations:

$$\sigma_I = 6{\cdot}31 \times 10^{-3} \exp(-0{\cdot}29\ \text{eV}/kT)\ \text{ohm}^{-1}\ \text{cm}^{-1}\ [300\text{-}600\ \text{K}], \tag{3}$$

$$\sigma_{II} = 3{\cdot}16 \times 10^{5} \exp(-1{\cdot}48\ \text{eV}/kT)\ \text{ohm}^{-1}\ \text{cm}^{-1}\ [600\text{-}1000\ \text{K}]. \tag{4}$$

The electrical conduction in solids are usually explained using band theory of solids according to which the variation of σ and θ in intrinsic semiconducting solids are given by the following expressions (Herman and Honing 1976)

$$\sigma_{\text{in}} = 2e\,[(2\pi kT)/h^2]^{3/2}\,(m_e\, m_h)^{3/4}\,(\mu_e + \mu_h) \exp[-E_g/2\,kT], \tag{5}$$

or

$$\sigma_{\text{in}} = \sigma_0(T) \exp(-Eg/2\,kT), \tag{6}$$

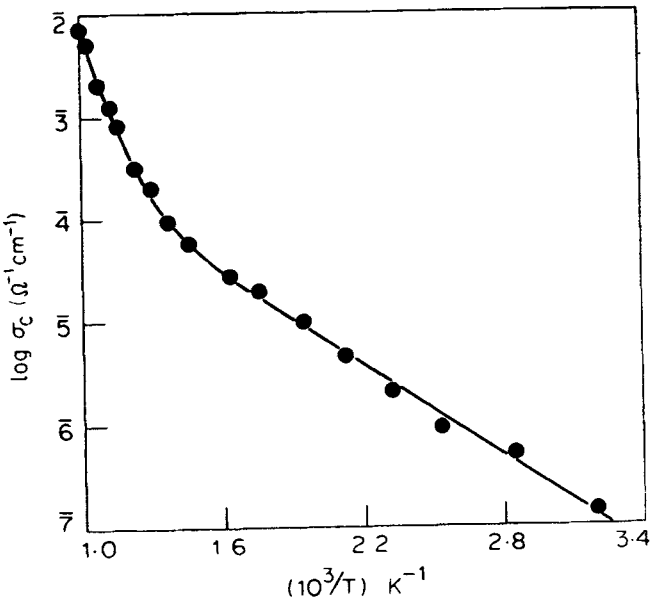

Figure 1. Variation of conductivity as a function of temperature of $CuWO_4$.

where $$\sigma_0(T) \equiv 2e\,[(2\pi\, kT)/h^2]^{3/2}\,(m_e\, m_h)^{3/4}\,(\mu_e + \mu_h), \tag{7}$$

and $$\theta = -\frac{Eg}{2e}\left(\frac{c-1}{c+1}\right)\frac{1}{T} - \frac{2k}{e}\left(\frac{c-1}{c+1}\right) - \frac{3k}{4e}\log_e(a), \tag{8}$$

or $$\theta = (n/T) + K, \tag{9}$$

where $$\eta = -\frac{Eg}{2e}\left(\frac{c-1}{c+1}\right), \tag{10}$$

$$K = -\left[\frac{2k}{e}\left(\frac{c-1}{c+1}\right) + \frac{3k}{4e}\log_e(a)\right], \tag{11}$$

$$C = \mu_e/\mu_h, \quad a = \frac{m_e}{m_h}.$$

k and h are Boltzman and Plancks constant, m_e, μ_e and m_h, μ_h are effective masses and mobilities of electron and hole respectively and Eg is the energy band gap of the solid. A plot of log σ vs $1/T$ and θ vs $1/T$ should yield straight lines under certain approximations. It can be seen from figures 1 and 2 that the curves are straight lines thus supporting the band conduction mechanism. It is easy to evaluate C and a from (9) to (11). From the evaluated values of C, a and $\sigma_0(T)$ and taking $m_h = 100\,m$ (m is free electron mass, we have taken $m_h = 100\,m$ bearing in mind narrow d-band hence localisation of holes in Cu^{2+}: $3d^9$ filled band) μ_h was estimated as 10^2 cm^2/V second which decreases with temperature. The mobility value and its variation with temperature supports the band conduction mechanism. It is thus concluded that the electrical conduction in $CuWO_4$ takes place *via* band mechanism.

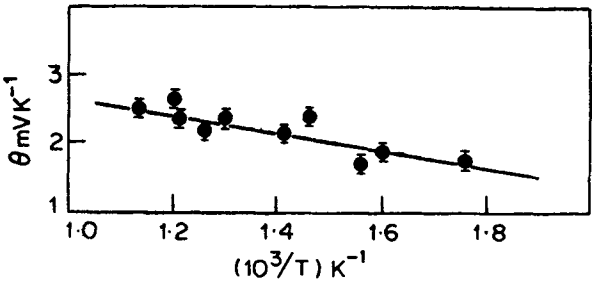

Figure 2. Variation of thermoelectric power as a function of temperature of $CuWO_4$.

To explain the conductivity data, one can consider the probable conduction mechanism as follows. In a transition metal compound the electrical conduction is mostly characterised by *d*-band near the Fermi surface. Since the *d*-electron wave function overlaps slightly with those of the nearest neighbour ions, they form very narrow energy bands (Adler and Feinleib 1970). The relevant bands for $CuWO_4$ are the filled O^{2-} : $2p$ band and empty W^{6+} : $5d$ band with a filled narrow Cu^{2+} : $3d^9$ $[t_{2g}^{(6)}\ e_g^{(3)}]$ band and an empty Cu^{2+} : $3d^1$ $[e_g^{(1)}]$ band. The empty $4s$ and $4p$ bands associated with Cu^{2+} ion are also important. Cu^{2+} : $3d$ sub-bands arise due to splittings by crystal and exchange fields (Brandow 1977). These narrow bands lie within $\sigma\sigma^*$ band gap i.e. within top of $2p$ filled band and bottom of $4s$, $4p$ and $5d$ empty bands. It can be understood by the behaviour of transition metal oxides in which the $2p$ band of oxygen ion is depressed by 5 eV from Fermi energy and the s-band, which in the transition metals overlap the *d* band in both the directions, is pushed up by 5 eV above Fermi energy (Adler 1968). It can therefore be said that two competing conduction processes exist in $CuWO_4$: conduction by hopping of charge carriers in the narrow $3d^9$ band and normal band-like conduction in the $2p$ band, dominating at lower and higher temperatures respectively. Since in this compound the $2p$-band is far below the Fermi energy, its contribution to conduction at low temperature seems negligible. In the transition metal compounds the mobility of charge carriers is very low at low temperature [*viz.* $\sim 0{\cdot}04$ cm^2/V sec.] due to the narrowness of *d*-band, therefore a polaron will be formed. Polaronic conduction is well discussed in the past few years (Appel 1968; Austin and Mott 1969; Bosman and van Daal 1970). It has an important role in the interpretation of transport properties of transition metal compounds. The formation of polaron takes place due to the interaction of slow moving electrons with the lattice. Unfortunately since the data related to the polaron coupling constant for this compound are not known, it is not possible to predict the type of polaron taking part in conduction. At high temperatures, the hopping conduction in the narrow $3d^9$ band is suppressed by the O^{2-} : $2p$ band conduction. At low temperatures conduction due to impurities cannot be ruled out.

The thermoelectric power is reported in the temperature range 550–900K and is calculated by using the relation

$$\theta = \Delta V / \Delta T. \tag{12}$$

The plot of θ vs $10^3/T$ (as shown in figure 2) is a straight line indicating the vali-

dity of the two-band model in high temperature range. The data can be summarised in the equation

$$\theta = [-1{\cdot}25\,(10^3 / T) + 3{\cdot}9]\ \text{mV/K}. \tag{13}$$

Since θ is positive, the compound is p-type. θ increases with temperature and this can be interpreted as follows. At low temperature the mobility of holes is very low *viz.* $\sim 0{\cdot}04$ cm^2/V sec and gives rise to low thermoelectric power. Above 500 K the mobility of the holes is quite large and decreases above 600 K with temperature. The increase of θ may be due to the onset of ionic conduction (probably the movement of oxygen ion vacancies) owing to the ionic nature of the compound.

The static dielectric constant ϵ' is measured at 1 kHz in the temperature range 300-1000 K. Figure 3 shows the variation of log ϵ' vs T. We have plotted log ϵ' just to accommodate the data. ϵ' increases slowly with temperature upto 600 K as is usual for ionic solids (Smyth 1955). This is due to lattice expansion, polarisability of the constituent ions due to increase in temperature and available volume together with the increase of atomic polarisability. The fast increase above 600 K is attributed to the thermally generated charge carriers. In most of the semiconducting compounds the number of charge carriers increases with temperature also. It seems that the mass of the charge carriers is quite large *viz.* $\sim 10^2$ m and the mobility of charge carriers decreases with temperature. If these charges are impeded by trapping a space charge polarisation builds up and macroscopic field distortion results (von Hipple 1954). This leads to a large increase in ϵ'. Lattice defects may also contribute to an increase in ϵ'.

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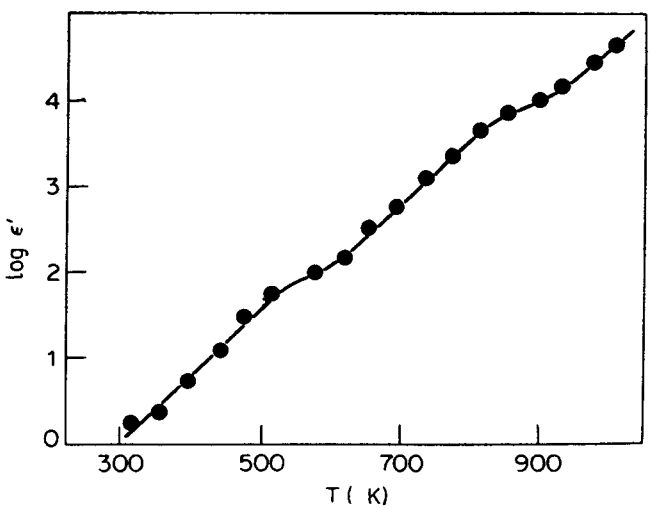

Figure 3. Variation of dielectric constant as a function of temperature $CuWO_4$.

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