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On electrical transport in $CoWO_4$ single crystals

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$CoWO_4$ is a p-type semiconductor with conductivity in the range 10^{-8} to 10^{-3} ohm^{-1} cm^{-1}. The solid exhibits extrinsic behaviour up to 750 K and intrinsic behaviour above 750 K. In this solid conduction by hopping of small polarons seems to be dominating up to 750 K and above 750 K conduction becomes band type. The energy band gap of the solid has been found to be 2.80 eV. The values of mobility and the mean free path are estimated. The variation of dielectric constant with temperature has been attributed to changes in atomic and ionic polarization and space charge polarization of thermally generated charge carriers.

1. Introduction

The electrical transport properties of transition metal compounds have drawn much attention in the last few years because of their complex electronic structures. These materials include the 3d-transition metal tungstates (TMT) [$MeWO_4$ where Me = Cr, Mn, Fe, Co, Ni and Cu etc.], having either Wolframite or Scheelite structure. Over the last few years we have been studying their electrical transport properties. To supplement the electrical transport studies of this series reported earlier [1, 2], the a.c. and d.c. electrical conductivity, thermoelectric power and static dielectric constant of $CoWO_4$ single crystal are reported in the present paper.

The crystal structure of $CoWO_4$ is of the $NiWO_4$ type [3]. The lattice parameters [4] are $a = 4.667$ Å, $b = 5.681$ Å, $c = 4.947$ Å and $\beta = 90°$, with errors estimated to be ± 0.001 Å and ± 0.02°. The crystallographic space group is $C^4_{2h}–P_{2c}$ [5] and the cell volume is 262.3 $Å^3$. The structure is monoclinic [4] with two formula units per unit cell and is characterized by zigzag chains of oxygen octahedra co-ordinating the metal ions and aligned along the *c*-axis. The magnetic moments are ferromagnetically aligned within the chains in the *ac*-plane, inclined to the *a*-axis by angles between 20 and 45° [6–8], and antiferromagnetically coupled to adjacent layers having a magnetic unit cell, which has twice the dimensions of the crystallographic unit cell along the *a*-axis [9]. The magnetic space group (Shubnikov group) [9] is $P_a 2/c$. It is antiferromagnetic with Neel temperature equal to 55 K [10], and magnetic moment equal to 3.6 ± 0.05 μm.

2. Experimental details

The single crystals of $CoWO_4$, used in our measurements, were grown by the flux method [11]. The crystals were identified by the X-ray powder method. The experimental details regarding the measurements and sample holder assembly are similar to our previous work [1]. The a.c. electrical conductivity and dielectric constant were measured with the help of Ruttonsna Simpson Universal, LCR Bridge Model 901-I (India), which operates at a frequency of 1 kHz. The d.c. electrical conductivity and thermoelectric power were estimated from the resistance and thermoelectromotive force values (emf), respectively, which were measured by a Philips (India) digital multimeter PM 2522/90, with an accuracy better than ± 0.25% and ± 0.20% in the case of resistance and emf measurements, respectively. The temperature of both the surfaces

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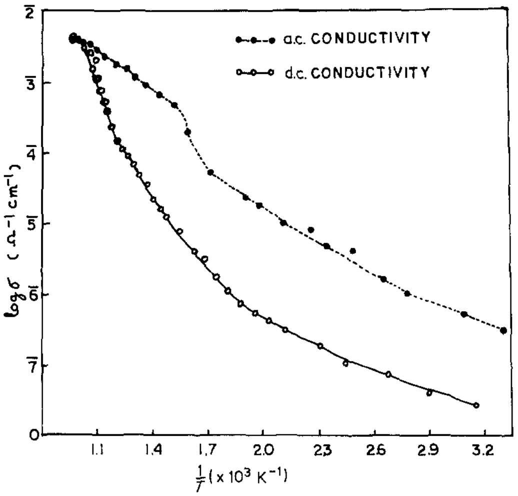

Figure 1 Variation of a.c. and d.c. electrical conductivity, $\sigma_{\text{a.c.}}$ and $\sigma_{\text{d.c.}}$, with temperature in a $CoWO_4$ single crystal.

of the crystal were measured with the help of chromel–alumel thermocouples attached to platinum electrodes. A temperature difference of $\Delta T \approx 20^\circ$ C was produced across the crystal. Ambient temperature has been taken as the average of the temperature of both surfaces.

3. Results

3.1. Electrical conductivity

The a.c. and d.c. electrical conductivities ($\sigma_{\text{a.c.}}$ and $\sigma_{\text{d.c.}}$) of $CoWO_4$ in the temperature range 300 to 1150 K are shown in Fig. 1. The variation of conductivity with temperature, can be expressed by the following expression [12]

$$\sigma = \sigma_0(T) \exp(-E_a/kT) \tag{1}$$

and

$$\sigma_0(T) = K' T^{3/2} a^{3/4} (1 + C) m_h^{3/2} \mu_h \tag{2}$$

where

$$K' = 2e\left(\frac{2\pi kT}{h^2}\right)^{3/2}, a = \left(\frac{m_e}{m_h}\right), C = \frac{\mu_e}{\mu_h},$$

where m_e, μ_e and m_h, μ_h are masses and mobilities of electrons and holes respectively and E_a is the activation energy. In view of Equation 2, the plot of $\log_{10}\sigma$ against $1/T$ should be a straight line. $\text{Log}_{10}\sigma_{\text{a.c.}}$ and $\log_{10}\sigma_{\text{d.c.}}$ against $10^3/T$ have been plotted and two straight lines in the temperature ranges 550 to 750 and 750 to 1150 K have been obtained. The activation energy and $\sigma_0(T)$ for both the temperature ranges are given in Table I.

TABLE I Electrical conductivity data of $CoWO_4$ in different temperature ranges

Temperature range (K)	$\sigma_0(T)$ (ohm cm)$^{-1}$	Activation energy (eV)
500–750	7.08×10^{-1}	0.64
750–1150	5.20×10^{4}	1.40

The activation energy in the temperature range 500 to 750 K is very small, 0.64 eV, thus it cannot be the activation energy for intrinsic conduction for $CoWO_4$ [13]. Therefore conduction below 750 K is due to impurities and defects etc. and is indicative of the extrinsic behaviour of the compound. The activation energy above 750 is 1.40 eV, which seems to be the activation energy for intrinsic conduction.

3.2. Thermoelectric power

The variation of thermoelectric power with temperatures from 300 to 1200 K for single crystal $CoWO_4$ is shown in Fig. 2. Thermoelectric power (θ) is calculated, using the relation

$$\theta = \frac{dE}{dT}. \tag{3}$$

Positive values of θ over the entire range of temperature studied have been obtained, establishing that the charge carriers in $CoWO_4$ are holes. Hence $CoWO_4$ is a p-type semiconductor. The thermoelectric power remains constant up to 750 K and then starts decreasing linearly with temperature. On a simple two band model, the temperature variation of θ may be given by the following expression [12]

$$-\theta = \frac{\eta}{T} + K \tag{4}$$

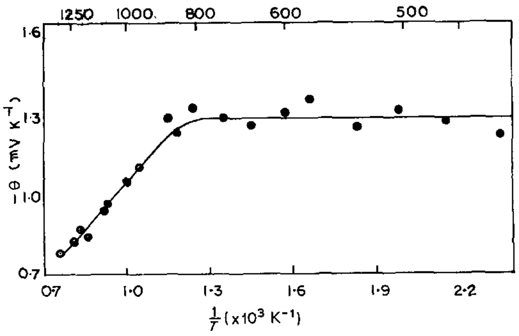

Figure 2 Variation of thermoelectric power, $-\theta$, with temperature for a $CoWO_4$ single crystal.

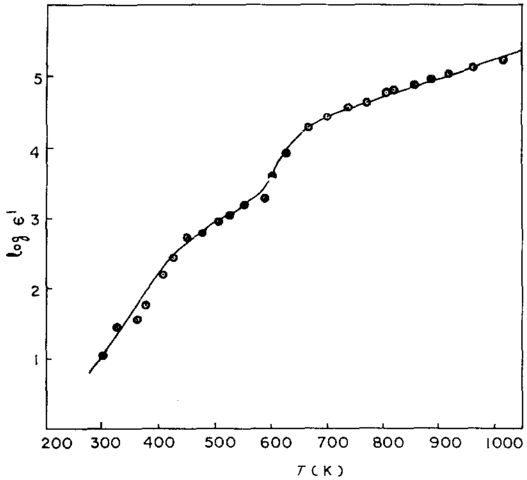

Figure 3 Variation of the static dielectric constant, ϵ', of a $CoWO_4$ single crystal with temperature measured at 1 kHz.

where

$$\eta = \frac{E_a}{e}\left(\frac{C-1}{C+1}\right) \qquad (5)$$

and

$$K = \frac{2k}{e}\left(\frac{C-1}{C+1}\right) + \frac{3k}{4e}\log_e(a). \qquad (6)$$

From the experimental values of η, K and E_a, one can estimate the values of C and a, and using these values of C and a besides the value of σ_0 (pre-exponential factor) in Equation 1, one can calculate the value of μ_h in terms of m_h^*. Since the exact value of m_h^* for this compound is not known, we have taken $m_h^* = 10m$ for the temperature range 300 to 750 K and $m_h^* = m$ for the temperature range 750 to 1200 K, where m is the free electron mass. The calculated value of μ_h for the higher temperature range is 63.9 $cm^2\,V^{-1}\,sec^{-1}$ (1200 K).

3.3. Static dielectric constant

The static dielectric constant ϵ' was measured on the same crystal. ϵ' was measured in the temperature range 300 to 1050 K. The plot of $\log \epsilon'$ against $1/T$ is shown in Fig. 3. ϵ' increases slowly up to 700 K. The increase is due to the ionic nature of the compound [15] (ionicity ≈ 0.80 [14]), the lattice expansion and the polarizability of the constituent ions. Besides these contributions, atomic polarizability [16] due to the loosening of bonds with increase in temperature also contributes to ϵ' to some extent. Above 700 K, the increase becomes fast and linear. This fast increase is due to the semiconducting nature of the compound above this temperature. Above 700 K, the number of thermally generated charge carriers, which are unable to move freely with electric field, increases. If these charges are impeded by trapping, a space charge builds up and macroscopic distortion results [15], thereby the ϵ' increases. This type of polarization which is known as space charge polarization, occurs when the number of charge carriers generated increase exponentially. All these charges take part in increasing the space charge polarization, therefore the dielectric constant increases at a much faster rate.

4. Discussion and interpretation of the experimental results

Thermoelectric power is constant over a temperature range 300 to 750 K. This indicates that the charge carrier concentration is constant. This property strongly favours the localized model for $CoWO_4$ below 750 K, i.e. charge carriers are localized at Co^{3+} sites. The estimated drift mobility from the conductivity, Seebeck coefficient [17] (for small polaron hopping) of 1.26×10^{-3} $cm^2\,V^{-1}\,sec^{-1}$ at (400 K) is very low. The mean free path (L) of the charge carriers calculated from the formula

$$L = \frac{3\mu}{4e}\cdot(2\pi mkT)^{\frac{1}{2}} \qquad (7)$$

is also very low, ~ 0.06 Å, which is much less than the lattice constant a [18]. According to Hill [19] for a single carrier dominated process, αeT, (where α is the thermoelectric power) should be equal to the activation energy of conduction. Applying this in this case it becomes obvious that the mid-temperature region is single carrier (Co^{3+}), impurity dominated, because we have obtained an αeT value approximately equal to 0.69 eV which is nearly equal to an activation energy (E_a) of 0.64 eV in this region. This indicates a polaron mechanism of conduction. In addition the ionic nature of the compound, narrow 3d-bands and the increase of electrical conductivity with frequency also suggest hopping conduction by small polarons [20]. The small polarons (Co^{3+} ions), present as a result of defects, give rise to p-type extrinsic conduction with thermally activated mobility which increases exponentially with temperature and is characterized by the following equation [21, 22]

$$\mu_d = \frac{A}{T^{3/2}}\exp(-E_m/kT) \qquad (8)$$

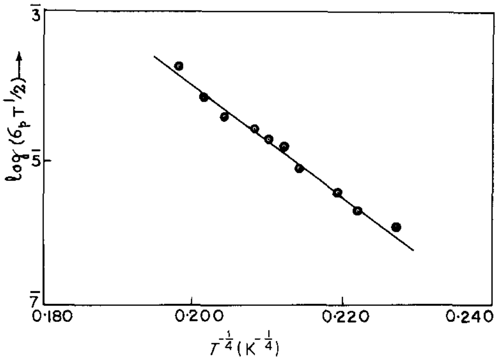

Figure 4 Log ($\sigma_\mathrm{p}T^{1/2}$) against $T^{-1/4}$ in a $CoWO_4$ single crystal.

where A is a constant and E_m is the activation energy for mobility. In hopping type conduction, small polarons move from one impurity centre (lattice site) to another by a thermally activated hopping process [23]. In the case of $CoWO_4$ hopping would involve electrons jumping from a Co^{2+} ion to a neighbouring Co^{3+} ion. In $CoWO_4$, since the 3d sub-bands (dϵ and dγ) are narrow, the electronic correlation will be strong, resulting in the formation of small polarons [24]. The conduction below 500 K follows Mott's equation [24, 25]

$$\sigma_\mathrm{p}T^{1/2} = A\exp(-B/T^{1/4}) \qquad (9)$$

where A and B are constants. It can be seen from Fig. 4 that the plot of log $\sigma_\mathrm{p}T^{1/2}$ against $T^{-1/4}$ is a straight line up to 500 K. Therefore it is concluded that conduction in the region 300 to 500 K is due to small polarons which conduct via a band type of hopping motion, while in the temperature range 500 to 750 K conduction is due to thermally activated small polaron hopping from one site to another neighbouring site.

Conduction between 750 and 1050 K is interpreted in the light of the band theory of solids. Higher E_a, μ_h and L values (1.40 eV, 63.9 cm^2 V^{-1} sec^{-1} and 84.1 Å respectively) and the decrease in mobility with temperature [26], together with the linear variation of log ϵ' with T and the smaller value of αeT (1.03 eV) than activation energy (E_a) (1.40 eV) are in favour of normal band type conduction. Appropriate bands for conduction are the filled O^{2-}: 2p and Co^{2+}: [$d\epsilon^3\alpha\ d\gamma^2\alpha\ d\epsilon^2\beta$] and empty Co^{2+}: $d\epsilon'\beta\ d\gamma^2\beta$, W^{6+}: 5d along with 4s, 4p bands associated with Co^{2+} ions. Ten-fold degeneracy of the d-orbitals is removed by crystal field and exchange splittings [27–29]. Each cation is surrounded by six anions with octahedral co-ordination [3]. The resulting octahedral crystal field splits the five spatially distinct orbitals into a lower triplet of dϵ symmetry (the xy, xz and yz orbitals) and an upper doublet of dr symmetry (the x^2-y^2 and $3z^2-r^2$ orbitals) [26, 27]. Their energy separation 10 Dq is $\approx$ 2 eV [27, 30]. Since in the higher temperature region conductivity contains a small contribution from a second carrier which is evident from the difference between αeT (1.03 eV) and activation energy (1.40 eV), in this case the band gap must be less than the true band energy unless there is clear evidence that the electron and the holes have significantly different mobilities. The value of $\mu_\mathrm{e}/\mu_\mathrm{h}$ (0.134) has been calculated from which it is obvious that electrons and holes have significantly different mobilities, therefore the true energy band gap for intrinsic conduction in this solid is approximately 2.80 eV. The value of the a.c. conductivity is larger below 800 K and approaches the d.c. value above 800 K and finally coincides with the d.c. value; this also supports the band model. The electrical conductivity above 1000 K becomes almost independent of temperature, so the conductivity behaviour may be said to approach to that of a degenerate semiconductor, in the sense that a large number of charge carriers give rise to high conductivity which is unaffected by the temperature [13].

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References

1. R. BHARATI, R. A. SINGH and B. M. WANKLYN, *J. Mater. Sci.* **15** (1980) 1293.
2. R. BHARATI, R. SHANKER and R. A. SINGH, *Pramana* (1980).
3. R. O. KELLING, *Acta Cryst.* **10** (1957) 209.
4. A. W. SLEIGHT, *ibid.* **B28** (1972) 2899.
5. B. F. ORMANT, *Strukturberich* **86** (1928–32), "Non-organic materials structures" (in Russian) GITTL, Moscow-Lenin Grad (1950).
6. H. WEITZEL, *Sol. Stat. Comm.* 8 (1970) 2071.
7. A. I. ZVYAGIN and E. N. KHATS'KO, *Sov. Phys. Sol. Stat.* **12** (1970) 258.
8. V. M. GREDESCUL, S. A. GREDESCUL, V. V. EREMENKO and V. M. NAUKEMOKO, *J. Phys. Chem. Sol.* **33** (1972) 859.
9. H. WEITZEL and H. LANGHOF, *J. Mag. Mag. Mater.* **4** (1977) 265.
10. L. G. VAN UITERT, R. C. SHERWOOD, H. J. WILLIAMS, J. J. RUBBIN and W. A. BONNER, *J. Phys. Chem. Sol.* **25** (1964) 447.

11. B. M. WANKLYN, *J. Mater. Sci.* 7 (1972) 813.
12. T. C. HERMAN and HONNING, "Thermoelectric Power and Thermomagnetic Effects and Applications", (McGraw-Hill, New York, 1976) p. 142.
13. G. V. SUBBARAO, B. M. WANKLYN and C. N. R. RAO, *J. Phys. Chem. Sol.* **32** (1971) 345.
14. K. HÜBNER, *Phys. Stat. Sol. (b)* **69** (1975) K1.
15. A. R. VON HIPPLE, "Dielectric Materials and Applications", (John Wiley, New York, 1954) p. 47.
16. C. P. SMYTH, "Dielectric Behaviour and Structure", (McGraw-Hill, New York, 1955) p. 132.
17. M. PRZYBYLSKI, A. GRAJA, A. RAJCHEL, M. GAWRON and T. BOROWIAK, *Phys. State. Sol.* (preprint).
18. A. J. BOSMAN and H. J. VAN DAAL, *Adv. Phys.* **19** (1970) 1.
19. R. M. HILL, *J. Phys. C* 9 (1976) L381.
20. D. ADLER and J. FEINLEIB, *Phys. Rev.* **B8** (1970) 3112.
21. T. HOLSTEIN, *Ann. Phys.* 8 (1959) 343.
22. L. FRIEDMAN and T. HOLSTEIN, *ibid.* **21** (1963) 494.
23. T. KASUYA, *J. Phys. Soc. Jap.* **13** (1958) 1096.
24. I. G. AUSTIN and N. F. MOTT, *Adv. Phys.* **18** (1969) 41.
25. H. SUMI, *J. Phys. Soc. Jap.* **33** (1972) 327.
26. S. METHFESSEL and D. C. MATTIS, in "Hand buch der Physik XVIII/I", edited by S. Flugge (Springer Verlag, Heidelberg, 1968) p. 389.
27. B. H. BRANDOW, *Adv. Phys.* **26** (1977) 715.
28. J. P. SUCHET, "Electrical Conduction in Solid Materials" (Pergman Press, Oxford, 1975) p. 47.
29. D. ADLER, *Rev. Mod. Phys.* **40** (1968) 714.
30. J. S. GRIFFITH, "The Theory of Transition Metal Ions", (Cambridge Press, London, 1961).

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