JOURNAL OF MATERIALS SCIENCE 27 (1992) 4003–4008

Electrical conduction in $CuWO_4$ crystals

T. MATHEW, N. M. BATRA, S. K. ARORA
Department of Physics, Sardar Patel University, Vallabh Vidyanagar 388 120, Gujarat, India

The d.c. electrical conductivity and thermoelectric power of $CuWO_4$ have been measured in the temperature range 300 to 700 K on unannealed and annealed single crystals and on polycrystalline pellets. It has been found that $CuWO_4$ is an n-type semiconductor. Relevant conduction mechanisms appropriate to the regions below and above 455 K are discussed on the basis of the experimental data on activation energy, mobility and carrier concentration.

1. Introduction

It is well known that the existence of magnetic ordering in the transition metal tungstate (TMT) family, having the general formula MWO_4 where M = Cu, Fe, Cd, Zn, etc., gives rise to an important modification of the energy spectrum of conduction electrons [1, 2]. Such a modification is likely to influence the electrical properties, such as the electrical resistivity, which in TMTs will have a greater value than in ordinary metals.

The present communication concerning $CuWO_4$, one of the prime members of the TMT family, describes a study of the d.c. electrical conductivity of unannealed and annealed single crystalline as well as polycrystalline samples in the temperature range 300 to 700 K, and the data obtained have been analysed in the light of various conduction mechanisms. The study also includes measurements of the thermoelectric power of the samples.

2. Experimental procedure

The crystals of $CuWO_4$ were grown by the flux method, the details of which have been described elsewhere [3]. For the present study, crystals of $CuWO_4$ were selected in the form of platelets of dimensions 4.0 mm × 2.0 mm × 0.6 mm. The d.c. electrical conductivity was measured with the help of a megohmmeter (EB M 115) and digital multimeter (MECO-7). The conductivity measurements were made by the two-probe technique, and the results were accurate to within 0.05%. The temperature was monitored using a Pt/Pt–10% Rh thermocouple. The investigations were made on four kinds of sample, namely (i) as-grown crystals, (ii) crystals annealed in air at 700 °C for 80 h, (iii) crystals annealed in an argon atmosphere at 700 °C for 80 h, and (iv) pelletized samples. The two surfaces of the sample in contact with steel electrodes were painted with silver paste, to ensure better electrical contact in the ceramic sample holder, as described elsewhere [4]. Powdered samples in the form of pellets were prepared using a hydraulic press and a suitable die with a pressure of 1124.91 kg cm^{-2}. The data of observations in this paper are the averages of the readings on five samples.

For thermoelectric measurements, the sample holder assembly schematically shown in Fig. 1 was employed. A thermal gradient was imposed across the sample by placing it between two Nichrome-wound heaters. A Chromel–Alumel thermocouple was used just behind the copper strips, and aluminium foil was used for contact with the sample. Copper wires were used as voltage probes. The entire system was kept in an evacuated glass chamber at a pressure of 10^{-5} torr, obtained by an oil rotary pump backed with a diffusion pump.

3. Results and discussion

The electrical conduction in solids is normally explained using the band theory, according to which the variation of electrical conductivity, σ, and thermoelectric power, θ, in intrinsic semiconducting solids are given [5] by the following expressions:

$$\sigma = \sigma_0(T)\exp\left(-\frac{E_g}{2kT}\right) \qquad (1)$$

where

$$\sigma_0(T) = 2e\left(\frac{2\pi kT}{h^2}\right)^{3/2}(m_e m_h)^{3/4}(\mu_e + \mu_h) \qquad (2)$$

and

$$\theta = \frac{\eta}{T} + A \qquad (3)$$

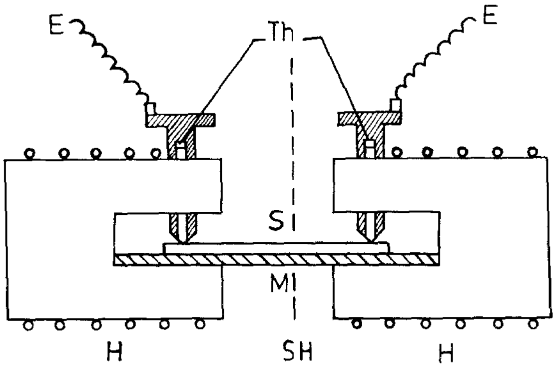

Figure 1 Sample holder assembly for thermoelectric power measurements: (M) mica sheet, (S) sample, (E) electrode, (H) heaters, (Th) thermocouple.

where

$$\eta = -\frac{E_g}{2e}\left(\frac{C-1}{C+1}\right) \quad (4)$$

$$A = -\left[\frac{2k}{e}\left(\frac{C-1}{C+1}\right) + \frac{3k}{4a}\ln a\right] \quad (5)$$

$$C = \frac{\mu_h}{\mu_e} \qquad a = \frac{m_h}{m_e} \quad (6)$$

k and h are the Boltzmann constant and Planck's constant, respectively, m_e, μ_e and m_h, μ_h are the effective masses and mobilities of electrons and holes, respectively, and E_g is the energy band gap of the solid. Then, knowing the Arrhenius plot (Equation 1), it is easy to calculate C and a from Equations 4 and 5 and thus μ_e can be calculated from the evaluated values of a, C and $\sigma_0(T)$, taking $m_h = 100m$ [6] and $m_e = 70m$ [7] (where m is the free electron mass); the basis of this approximate choice is that the material has a narrow d-band and the holes are localized in the Cu^{2+} $3d^9$ filled band. Consequently, we can calculate the carrier concentration n and the lifetime τ_e using the relations

$$\sigma = n_e\mu_e \quad (7)$$

and

$$\tau_e = \frac{1}{e}m_e\mu_e \quad (8)$$

The values of μ_e, n_e and τ_e so obtained have been summarized in Table I.

The measured Arrhenius data of d.c. conductivity versus temperature are shown graphically in Fig. 2 for different samples. The case of the pellet and that of the as-grown crystal distinctly show two regions, namely the intrinsic region (above 455 K) and the extrinsic region (below 455 K). These results can be summarized by the representative equations given in Table II.

The conductivity data for semiconducting materials are generally explained using either or both of the band model or localized model and the large-polaron model, etc. [8, 9]. However, before applying a model one has to know the electrical energy bands of the compounds involved. The electronic properties of transition metal compounds are mostly characterized by a d-band near the Fermi surface. It is also known that the 2s and 2p orbitals of oxygen strongly overlap with the 4s and 4p orbitals of 3d transition metal ions. This overlapping entails a strong hybridization, leading to a large energy gap between the top of the 2p band and the bottom of the 4s and 4p bands. In the transition metal compounds, the mobility of charge carriers is very low (Table I) even at lower temperature (up to 455 K) due to the narrowness of the d-band, so that a polaron is likely to be formed by the interaction of slow-moving electrons with the lattice [10–14]. But, 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 lower temperatures (up to 455 K), the conduction is therefore believed to be due to impurities; thus the possibility of hopping conduction cannot be ruled out.

TABLE I Values of μ_e, τ_e and n_e determined at 350 K

Sample	μ_e ($m^2 V^{-1} s^{-1}$)	τ_e (s)	n_e (m^{-3})
As-grown crystal	4.760×10^{-17}	1.897×10^{-26}	2.227×10^{26}
Pellet	3.848×10^{-16}	1.534×10^{-25}	5.007×10^{26}

The extrinsic regions below 455 K have slopes (Fig. 2) which correspond to the activation energy of the as-grown crystal and the pellet; these are calculated to be 0.062 and 0.259 eV, respectively. The lower value of activation energy in the case of the as-grown crystal suggests that

(i) the charge carriers for conduction are not thermally generated but are constants,

(ii) the extrinsic conduction is governed by native defects or interstitials and impurities, and

(iii) the electrical conduction might occur through ionized impurity centres or may be through polaronic motion.

The band-type conduction of ionized impurity centres contributes to conductivity according to the relation [15]

$$\sigma_{dc} = \sigma_0(T)\exp\left(-\frac{E_i}{2kT}\right) \quad (9)$$

where E_i is identified as the ionization energy of donors or acceptors (usually $E_i \simeq 0.1$ eV). Now, compared to the crystal, the conduction mechanism in the pellet appears to be different, because the latter has a relatively higher value of activation energy (0.259 eV). Thus band-type conduction is possible for the case of the pellet, but not the crystal. The alternative is to consider small polaron conduction below 455 K in the case of the as-grown crystal. The fact that narrow-band, low-mobility semiconductors like transition-metal or rare-earth oxides exhibit a strong coupling between charge carriers and lattice vibrations [11] supports a small-polaron hopping conduction here. The contribution of a small-polaron hopping mechanism towards electrical conductivity is given by the relation [11, 12]

$$\sigma T^{1/2} = \sigma_0(T)\exp(-W_H/kT) \quad (10)$$

where W_H is the small-polaron hopping energy. Consequently, the plot of $\ln(\sigma T^{1/2})$ against $10^3/T$ at temperatures below 455 K for the as-grown crystal shows a straight line (Fig. 3); the hopping energy calculated from the slope of the curve is 0.082 eV. This polaron hopping energy is in reasonable agreement with the activation energy (0.062 eV) calculated below 455 K from Fig. 2 for the as-grown crystal. Therefore one is inclined to conclude that the electrical conduction in $CuWO_4$ crystals below 455 K may be due to a small-polaron hopping (sph) mechanism, and the activation is entirely due to thermally increased mobility, given by the relation [13, 16]

$$\mu_{sph} = \frac{\mu_0}{T^{3/2}}\exp\left(-\frac{E_m}{kT}\right) \quad (11)$$

where E_m is the activation for the mobility change. As a result of small-polaron hopping via lattice defects,

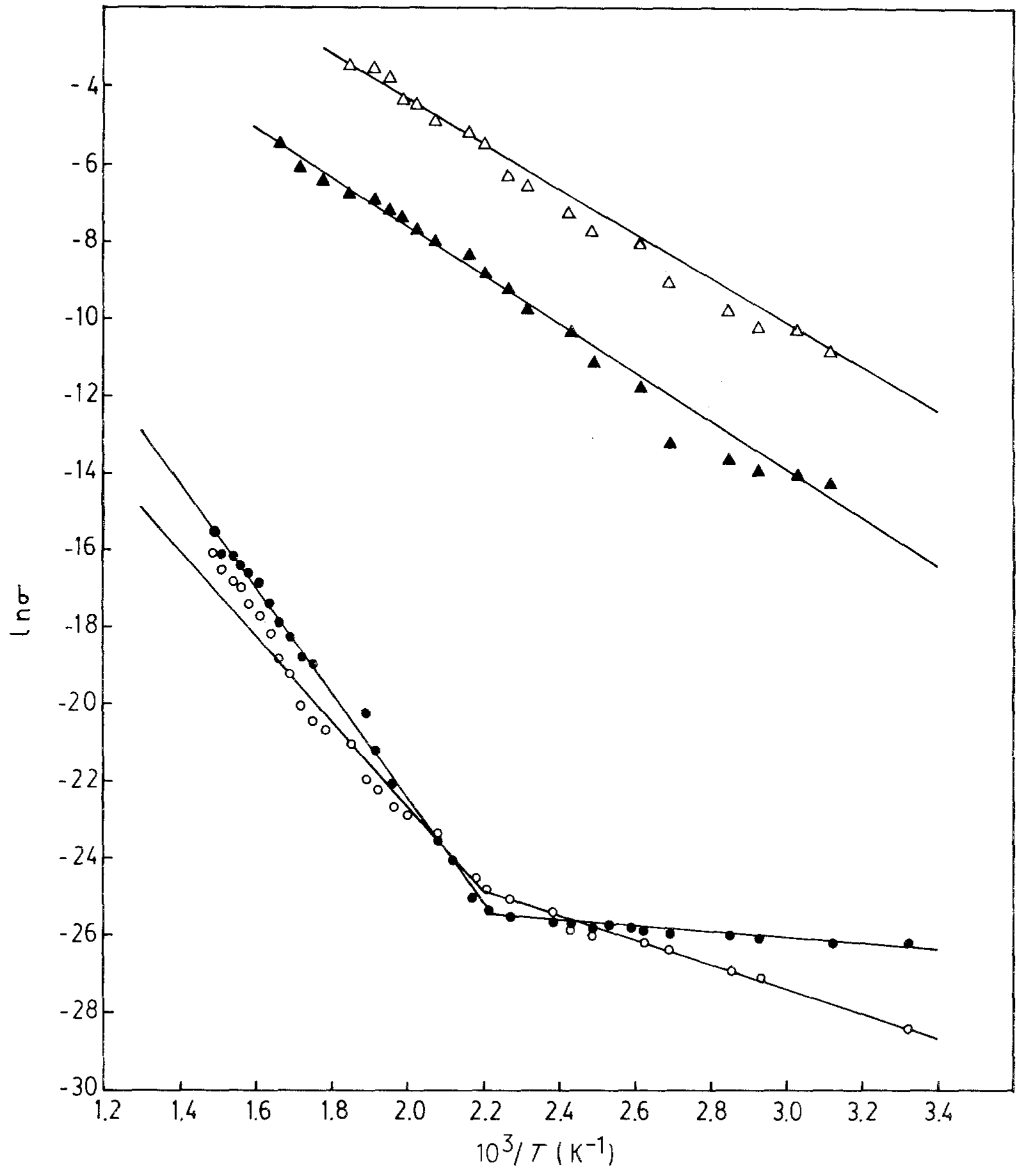

Figure 2 Variation of electrical conductivity (ln σ) against reciprocal temperature ($10^3/T$) in $CuWO_4$: (●) as-grown crystals, (▲) air-annealed crystals, (○) pellet, (△) argon-annealed crystals.

TABLE II Representative equations for the two regions of conduction in $CuWO_4$

Sample	Extrinsic region (below 455 K)	Intrinsic region (above 455 K)
As-grown crystals	$\sigma_{ex} = 2.79 \times 10^{-11} \exp(-0.06/kT)$	$\sigma_{in} = 1.12 \times 10^{-5} \exp(-1.17/kT)$
Pellet	$\sigma_{ex} = 3.41 \times 10^{-10} \exp(-0.26/kT)$	$\sigma_{in} = 1.12 \times 10^{-6} \exp(-1.06/kT)$

interstitials and impurities, the charge carrier concentration remains constant up to a certain temperature and hence the increase in electrical conductivity is essentially due to increase in the mobility of charge carriers with temperature.

The intrinsic nature of the compound is observed to arise above 455 K, the activation energy measured from Fig. 2 being 1.18 eV for the as-grown crystal and 1.06 eV for the pellet. Owing to these relatively higher values of the activation energy and the electrical resistivity ($\simeq 10^{10}$ Ω cm) it seems probable that the electrical conduction is brought about by an electron transferred from one Cu^{2+} to the adjacent Cu^{2+} ion. Such a transfer would lead to the formation of Cu^{3+} ions:

$$Cu^{2+} + Cu^{2+} \rightarrow Cu^{3+} + Cu^{+}$$

This process needs quite a lot of energy, because both Cu^{3+} and Cu^{+} ions are less stable than Cu^{2+}. Evidently, in this region (above 455 K) the conduction by excitation of electron from the valence band to the nearer conduction band seems more probable.

However, according to Suchet [17] a compound containing either empty or completely filled 3d sub-levels cannot tend itself to transfer. Now, the activation energy in this temperature range (455–700 K) for the as-grown crystal is 1.17 eV and hence the energy gap is expected to be 2.34 eV. But according to

Bharati *et al.* [6], the energy gap between the O^{2-}:2p filled band and the empty Cu^{2+}:3d band in $CuWO_4$ is 2.96 eV ($\simeq$ 3 eV) in this temperature range. Therefore, the estimated values of activation energy cannot be assigned as the activation energy for O^{2+}:2p $\rightarrow Cu^{2+}$:3d ($E_g \downarrow$) type conduction. This is, however, more likely to be the energy required to excite an electron from the 3d valence band to the empty 3d band. Further, the lower value of the mobility (Table I) indicates the formation of some kind of polarons. This, of course, seems quite reasonable because the presence of narrow 3d bands may lessen the activation energy to some extent. The activation energy is reduced to an amount which is equal to the polaron binding energy; such polarons conduct according to the relation

$$\sigma = \sigma_0(T)\exp\left(-\frac{E_a + \hbar W_0}{kT}\right) \qquad (12)$$

where $\hbar W_0$ is the polaron binding energy. Obviously, the actual activation energy is less than the estimated value. The drop in activation energy around 455 K appears to be due to a change in the conduction mechanism. One might therefore argue that large or intermediate mobility polarons change into small polarons. The low-mobility polarons do not contribute appreciably to the electrical conduction which results in a decrease in the activation energy.

On the other hand, the annealed samples (Fig. 2), show only one region as against two in the unannealed and the pelletized samples. The activation energy is found to be 0.495 and 0.545 eV for argon- and air-annealed samples, respectively. Due to the greater value of activation energy as compared to ionization energy (0.1 eV), small-polaron hopping conduction does not seem probable, while large or small polaron as well as normal band conduction may be responsible for the electrical conduction.

The activation energy computed from the $\ln(\sigma T^{1/2})$ versus $10^3/T$ plots (Fig. 3) is found to be 0.492 and 0.544 eV for argon- and air-annealed samples, respectively. The values worked out from Figs 2 and 3 are nearly the same for the same kind of the sample. Therefore, it seems that small or large polaron band type conduction is probable and not the sph conduction.

The observation on the annealed samples is interesting. In fact, the annealing is known to be characterized [18] by small changes in particle size and dislocation density along with large changes in twin probability and electrical resistivity. The surface texture changes from coarse to smooth, the defects being annealed out, and hence it might be thought that a lowering of the resistivity would result, as observed (Fig. 2), signifying a greater degree of reflection of electrons from the surface after annealing. Further, the

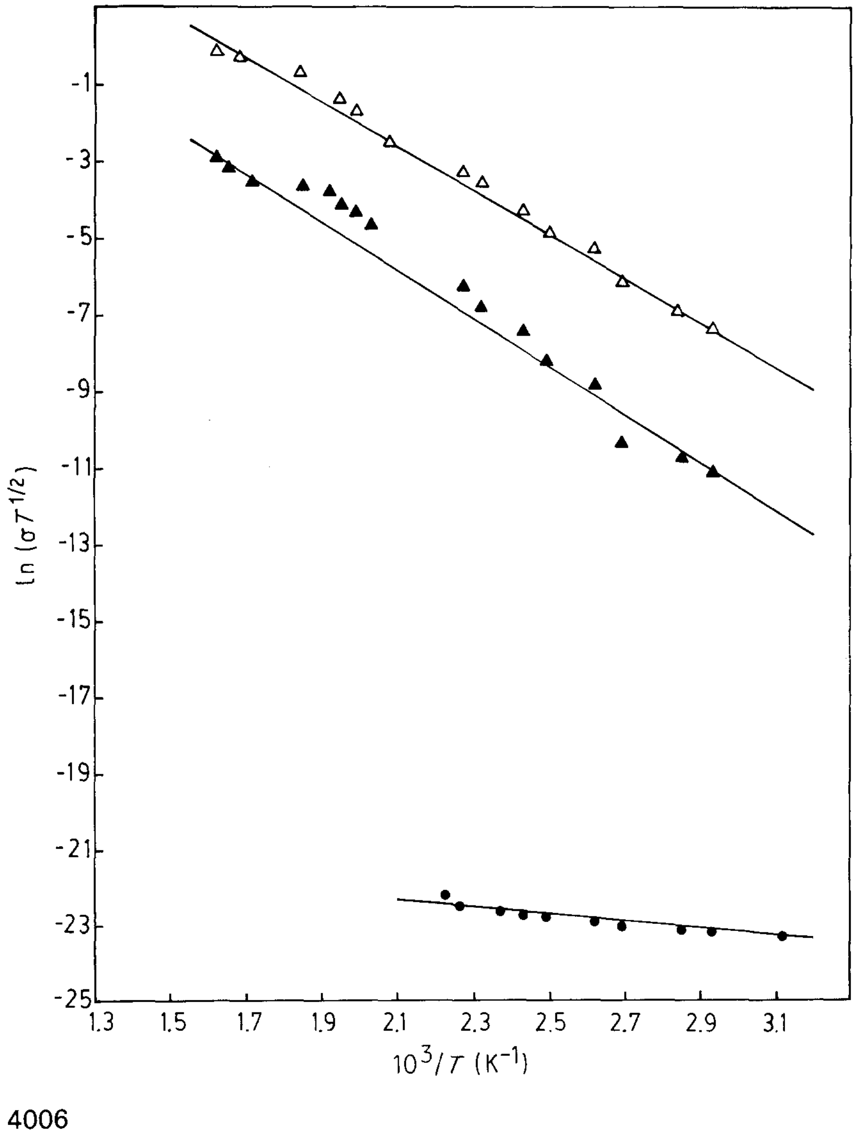

Figure 3 Variation of $\ln(\sigma T^{1/2})$ against reciprocal temperature ($10^3/T$) in $CuWO_4$: (●) as-grown crystals, (▲) air-annealed crystals, (△) argon-annealed crystals.

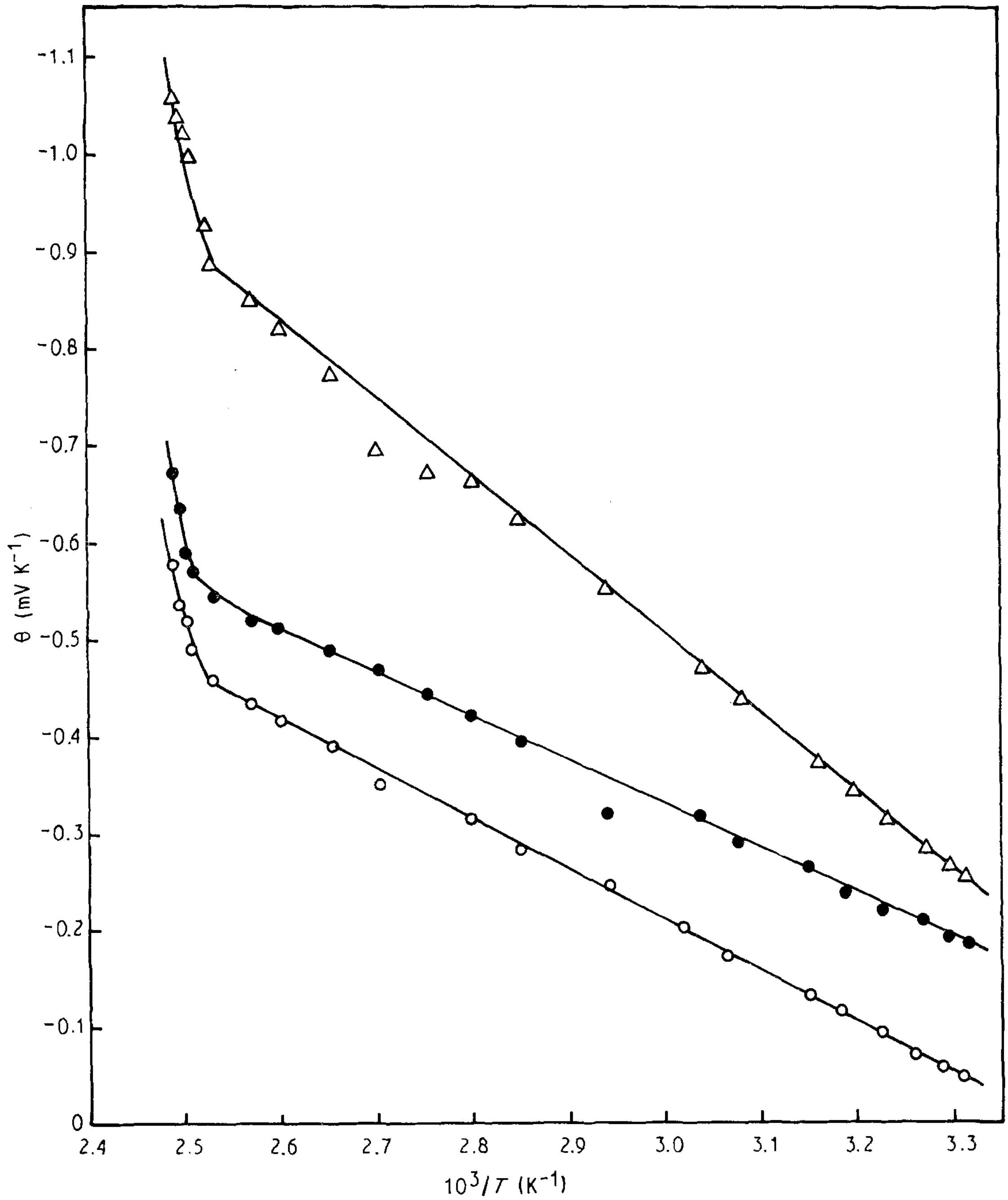

Figure 4 Variation of thermoelectric power, θ, against reciprocal temperature ($10^3/T$) in $CuWO_4$: (○) pellet, (△) argon-annealed crystals, (●) as-grown crystals.

influence of argon gas compared to air favoured the formation of dipoles by interstitial and substitutional ion pairs, thereby leading to a dipole concentration and vacancy states. This gives rise to oxygen vacancies which are compensated by cationic reduction. Obviously therefore, the argon annealed crystal shows lesser resistivity, as observed, compared to the air annealed crystal.

The variation of thermoelectric power θ measured as a function of $10^3/T$ is shown in Fig. 4. That θ is observed to be negative over the entire range of temperatures reveals the n-type nature of $CuWO_4$. The behaviour of the three kinds of sample is fairly similar, as seen from Fig. 4. At lower temperatures the mobility of electrons is very low, entailing low thermoelectric power, the sharp deflection of thermoelectric power at 396 K being due either to the presence of the narrow 3d sub-bands (there is a possibility of large-polaron formation in the wide O^{2-}:2p band that conducts via a band mechanism) or to the movement of oxygen ion vacancies owing to the ionic nature of the compound.

4. Conclusions

1. Observations on the electrical conductivity and thermoelectric power reveal the n-type character of $CuWO_4$.

2. A change in the conduction mechanism is noticed to occur at 455 K in the case of as-grown crystals and pellets. There is extrinsic conduction below 455 K and intrinsic conduction above 455 K.

3. Below 455 K in the case of single crystals, conduction is thought to be due to a small-polaron hopping mechanism while in the case of pellets the normal band-type conduction is appropriate. Above

455 K, in both samples, large-polaron as well as normal band conduction seems responsible for electrical conduction.

4. In the case of annealed samples there exists one region of conduction for which large-polaron as well as normal band conduction seems more relevant.

Acknowledgement

One of the authors (T. M.) is grateful to the CSIR, New Delhi, for financial assistance.

References

1. D. ADLER, *Rev. Mod. Phys.* **40** (1968) 714.
2. K. C. LI and C. YU. WANG, "Tungsten" (Chapman and Hall, London, 1956).
3. S. K. ARORA, T. MATHEW and N. M. BATRA, *J. Crystal Growth* **88** (1988) 379.
4. G. S. T. RAO, PhD thesis, Sardar Patel University (1982).
5. T. C. HERMANN and J. M. HONING, "Thermoelectric Power and Thermomagnetic Effects and Applications" (McGraw-Hill, New York, 1976) p. 142.
6. R. BHARATI, R. SHANKER and R. A. SINGH, *Pramana* **14** (1980) 449.
7. J. P. DOUMERE, J. HEJTMANEK, J. P. CHAMINADE, M. POUCHARD and M. KRUSSANOVA, *Phys. Status Solidi (a)* **82** (1984) 285.
8. O. PRAKASH, *Proc. Ind. Acad. Sci.* **87A** (1978) 331.
9. C. N. R. RAO and K. P. R. PISHARODY, *Progr. Solid State Chem.* **10** (1974) 207.
10. H. G. REIK, in "Conduction in Low Mobility Solids", edited by N. Klein, D. N. Taunhauser and M. Pollack (Taylor and Francis, London, 1971).
11. J. APPEL, *J. Solid State Phys.* **21** (1968) 193.
12. I. G. AUSTIN and M. F. MOTT, *Adv. Phys.* **18** (1969) 41.
13. A. G. BOSMAN and H. J. VAN DAAL, *ibid.* **19** (1970) 1.
14. G. H. JOENKER and S. VANHOUTEN, "Halbteiter Probleme" (Braunschweig, Vieweg, 1961) p. 118.
15. A. J. DEKKER, "Solid State Physics" (Macmillan, London, 1964) p. 305.
16. I. K. NAIK and T. Y. TIEN, *J. Phys. Chem. Solids* **39** (1978) 311.
17. J. P. SUCHET, "Electrical Conduction in Solid Materials" (Pergamon, Oxford, 1975) p. 147.
18. A. GANGULE, *J. Appl. Phys.* **43** (1972) 3943.

Received 20 September 1990
and accepted 7 March 1991