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Electrical conductivity of single crystal nickel tungstate

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Measurements of a.c. and d.c. electrical conductivity in crystals of nickel tungstate, in the temperature range 300 to 1100 K, are presented. $NiWO_4$ is found to be a semiconductor with a band gap of 2.10 eV. The nature of the electrical conduction is discussed in the light of various conduction models.

1. Introduction

Because of the interesting physical properties and the industrial importance of the transition metal oxides, their magnetic, optical, structural and thermophysical behaviour has been extensively investigated. The electrical properties of single crystals of nickel tungstate have not yet been reported, although the electrical properties of some metal tungstates have been published [1–4], and we have reported out study of electrical conductivity and thermoelectric power in $NiWO_4$ pressed pellets [2, 3]. In this paper, we report studies of electrical conduction in $NiWO_4$ single crystals.

2. Sample and experimental techniques

The crystals were grown by the flux growth technique [5] and the furnace used for crystal growth in air, as well as under reducing conditions, has been described previously [6]. The starting materials were of BDH* Laboratory reagent grade. Hot-pouring techniques were used to separate single crystals from the molten flux. The crystal products were identified by the X-ray powder method.

Electrical conductivity was measured by the two-electrode method. The a.c. electrical conductivity was determined by recording the resistance, using an LCR bridge (Ruttonsha Simpson Universal Bridge Model 901-I, India) which works at an internal frequency of 1 kHz. The accuracy in the resistance measurement is ± 1.25% of the reading and ± 0.25% of the full scale range. The d.c. electrical conductivity was determined by measuring the resistance by Digital Multimeter PM2522/90, (Philips, India). The accuracy in the resistance measurement is ± 0.37% of the reading and ± 0.2% of the range. Other details are described in our previous publications.

3. Results and discussion

Alternating current and direct current electrical conductivity measurements on single crystal $NiWO_4$ have been made in the temperature range 300 to 1100 K. Log $\sigma_{a.c.}$ and log $\sigma_{d.c.}$, plotted against $1/T$, are shown in Fig. 1. Both curves show a positive slope below 400 K and a broad minimum near 400 K. This behaviour indicates the presence of water molecules and hydrate formation and suggests that the compound is hygroscopic. The curve for $\sigma_{d.c.}$ against $1/T$ is linear, in accordance with the well-known exponential relation $\sigma = \sigma_0 \exp(-W/kT)$. The curve is represented by the following equation in the temperature range 500 to 750 K;

$$\sigma_{a.c.} = 9.33 \times 10^3 \exp\left(-\frac{1.05\,\text{eV}}{kT}\right) \text{ohm}^{-1}\,\text{cm}^{-1}. \quad (1)$$

Above 750 K the curve is represented by

$$\sigma_{d.c.} = 7.06 \times 10^{-1} \exp\left(-\frac{0.45\,\text{eV}}{kT}\right) \text{ohm}^{-1}\,\text{cm}^{-1}. \quad (2)$$

*BDH – British Drug House.

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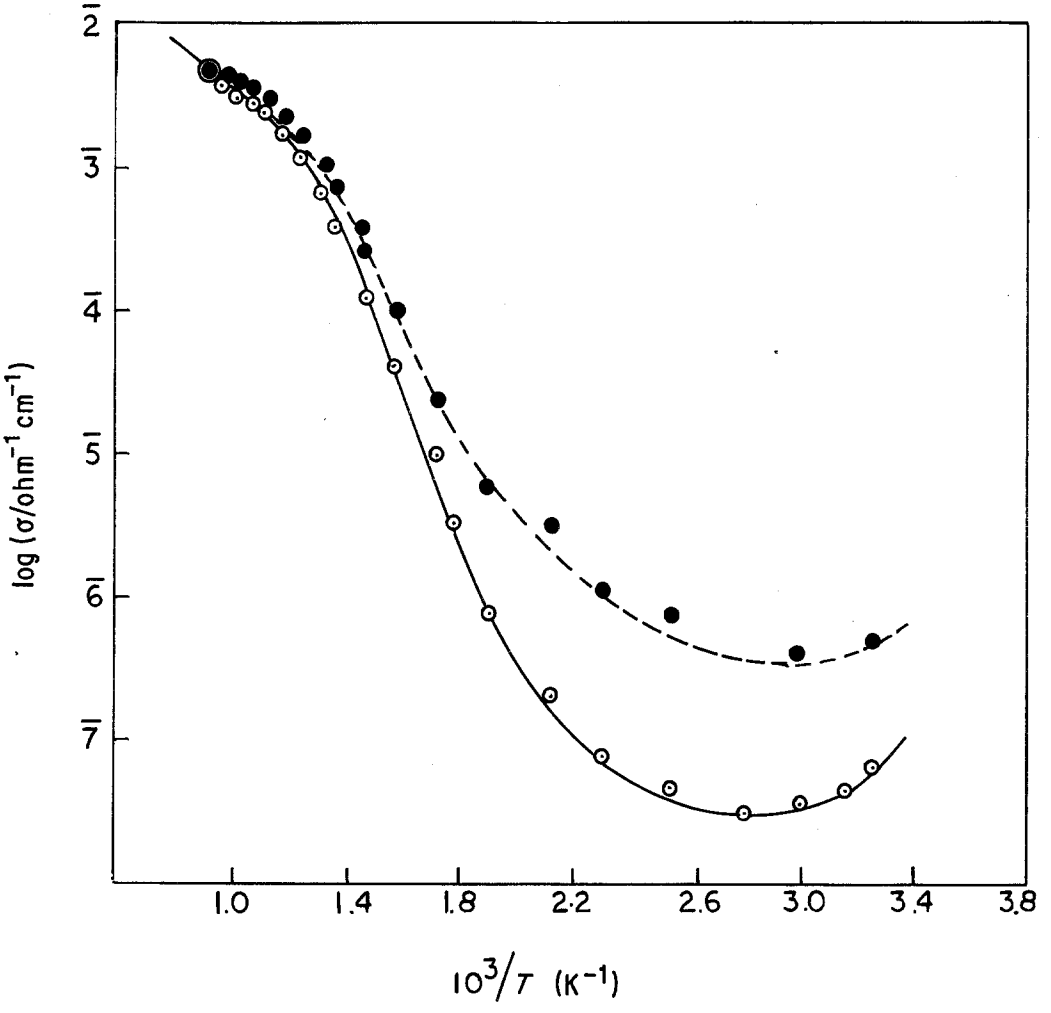

Figure 1 Variation of conductivity as a function of temperature in $NiWO_4$. (Solid circles indicate a.c. conductivity; open circles d.c. conductivity.)

The electrical conductivity above 500 K can be explained by the band theory of solids. The valence band in this material includes the filled O^{2-}:2p and Ni^{2+}:$3d^8$ ($t_{2g}\uparrow\downarrow^6 e_g\uparrow^2$) bands, and the conduction band includes unoccupied Ni^{2+}:$3d^2$ ($e_g\downarrow^2$), Ni^{2+}:4s, 4p and empty W^{6+}:5d bands. The Ni^{2+} 3d-sub-bands arise from the crystal field and exchange splittings [7]. These narrow bands lie within the O^{2-}:2p and W^{6+}:5d bands [8]. Because of the electronic structure and band formation in $NiWO_4$, the following two types of conduction mechanisms can be considered; (i) conduction by the transfer of 3d-electrons between neighbouring metal ions and (ii) conduction by the excitation of an electron from the valence bands to the nearer conduction band.

For the first type of conduction mechanism, nickel ions must exist in two ionization states, located at similar crystallographic sites [9]. It is well known that pure nickel oxide is an oxygen-excess semiconductor and the permanent defects are metal vacancies. A nickel cation vacancy produces two acceptor states (holes): Ni^{3+}–V_M^-–Ni^{3+}, where V_M is a cation vacancy. A Ni^{3+} ion thus introduced into the crystal jumps from one Ni^{2+} site to another. But if such defects are present in $NiWO_4$, one should obtain a higher value of conductivity at room temperature (Sabane *et al.* 1966 [10]) than we have found ($\approx 10^{-8}$ ohm^{-1} cm^{-1}). This indicates that the $NiWO_4$ single crystal which we have used in our measurements does not have such defects and only Ni^{2+} ions are present; thus this kind of transfer mechanism can be ruled out. The second type of electron transfer, which is more probable, can be considered as follows. Owing to the high resistivity ($\approx 10^8$ ohm cm) and

activation energy (1.05 eV) it seems likely that an electron may be transferred from one Ni^{2+} to the adjacent Ni^{2+} ion [10]. Such a transfer will lead to the formation of Ni^{3+} ions: $Ni^{2+} + Ni^{2+} \rightarrow Ni^{3+} + Ni^{+}$. This process needs high energy, because both Ni^{3+} and Ni^{+} ions are less stable than Ni^{2+}. Hence it seems most probable that conduction is due to this mechanism in the temperature range 500 to 750 K.

But, according to Suchet [11], whenever a compound contains either empty or completely filled 3d-sublevels, it cannot lend itself to transfer. Now, we consider the second type of conduction mechanism. The activation energy in this temperature range is 1.05 eV and hence the energy band gap will be 2.10 eV. If we assume 2.10 eV to be the band gap in $NiWO_4$, we can say that intrinsic conduction occurs in this temperature range. But according to several other workers [12, 13], the energy gap between the O^{2-}:2p filled band and the empty Ni^{2+}:3d band for NiO is about 3.6 eV in the temperature range 700 to 1200 K. Therefore, the activation energy estimated by us cannot be assigned as the activation energy for O^{2-}:2p $\rightarrow Ni^{2+}$:3d ($e_g\downarrow^2$) type conduction. It is more likely to be the energy required to excite an electron from the 3d-valence band to the empty 3d-band. The lower value of mobility (about 0.47 $cm^2\,V^{-1}\,sec^{-1}$) obtained by combining the electrical conductivity and thermoelectric data [2] indicates the formation of some kinds of polarons [14] in this temperature range. This 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 equal to the polaron binding energy, since such polarons conduct according to the relation

$$\sigma = \sigma_0 \exp\left(-\frac{E_a + \hbar\omega_0}{kT}\right) \qquad (3)$$

where $\hbar\omega_0$ is the polaron binding energy. Therefore, the actual activation energy will be less than the estimated value. The drop in activation energy above about 750 K appears to be due to a change in the conduction mechanism in view of the lower value of the mobility (about 1.22×10^{-2} $cm^2\,V^{-1}\,sec^{-1}$). It is argued that the polarons of large or intermediate mobility change into small polarons. Low values of the low mobility polarons, correspond to thermally activated hopping of localized small polarons [15]. The low mobility polarons become almost stable and do not contribute considerably to the electrical conduction, and this is in agreement with the theory given by Toyozawa [16]. This results in a decrease in the activation energy.

The a.c. conductivity is found to be higher than the d.c. conductivity below 800 K. Therefore, one can expect that electronic as well as ionic contributions are present in $\sigma_{a.c.}$. Above 800 K, $\sigma_{a.c.}$ and $\sigma_{d.c.}$ coincide, indicating that the electronic charge carrier mobility and concentration become much larger than the mobility and the concentration of the free ions. Hence, the ionic contribution becomes negligible, and therefore, $\sigma_{a.c.}$ becomes entirely electronic above 800 K.

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References

1. R. BHARATI, R. SHANKER and R. A. SINGH, *Pramana* **14** (1980) 449.
2. R. BHARATI, R. A. SINGH and B. M. WANKLYN, *J. Mater. Sci.* **15** (1980) 1293.
3. *Idem, ibid.* **16** (1981) 775.
4. R. BHARATI and R. A. SINGH, *ibid.* **16** (1981) 511.
5. B. M. WANKLYN, *ibid.* 7 (1972) 813.
6. G. GARTON, S. H. SMITH and B. M. WANKLYN, *J. Cryst. Growth* **13/14** (1972) 588.
7. B. H. BRANDOW, *Adv. Phys.* **26** (1977) 651.
8. D. ADLER, *Rev. Mod. Phys.* **40** (1968) 193.
9. I. BRANSKY and N. M. TALLAN, *J. Chem. Phys.* **49** (1968) 1243.
10. C. D. SABANE, A. P. B. SINHA and A. B. VISWAS, *Ind. J. Pure Appl. Phys.* **4** (1966) 187.
11. J. P. SUCHET, "Electrical Conduction in Solid Materials" (Pergamon Press, Oxford, 1975) p. 47.
12. Y. M. KSENDZOV and I. A. DARKIN, *Sov. Phys. (Solid State)* 7 (1965) 1519.
13. S. PIZZINI and R. MORLOTTI, *J. Electro. Chem. Soc.* **114** (1967) 1179.
14. H. G. REIK, "Conduction in low mobility solids", edited by N. Klein, D. N. Taunhauser and M. Pollack (Taylor and Francis Ltd., London, 1971).
15. G. H. JONKER and S. VANHOUTEN, "Halbteiter Probleme" (Braunschweig, Vieweg, 1961) p. 118.
16. Y. TOYOZAWA, *Prog. Theor. Phys.* **26** (1961) 26.

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