

## LETTER TO THE EDITOR

### On electrical conduction in reduced rutile

A number of studies on electrical conduction in reduced rutile have been made <sup>1) 2)</sup> <sup>3) 4) 5)</sup> but still uncertainties concerning the interpretation of electron mobility and electron statistics have remained. Frederikse <sup>2)</sup> deduced effective masses of 12-30  $m_e$  from Seebeck and Hall data on rather strongly reduced material. In a previous paper <sup>5)</sup> the present authors reported Hall-measurements on slightly reduced material. The mobility perpendicular to the  $c$ -axis was found to be independent of the amount of reduction, but the behaviour of the Hall-coefficient did depend on it. Donor interaction was suggested, but it should be noted that the presence of compensating impurities ( $Al^{3+}$  <sup>6)</sup>,  $Fe^{3+}$ ) may not be negligible.

In this note we report on the conductivity and Hall-effect ( $j \perp C$ ,  $H \parallel C$ ) of reduced rutile crystals doped with about 100 p.p.m.  $Al_2O_3$ . The boules were obtained from

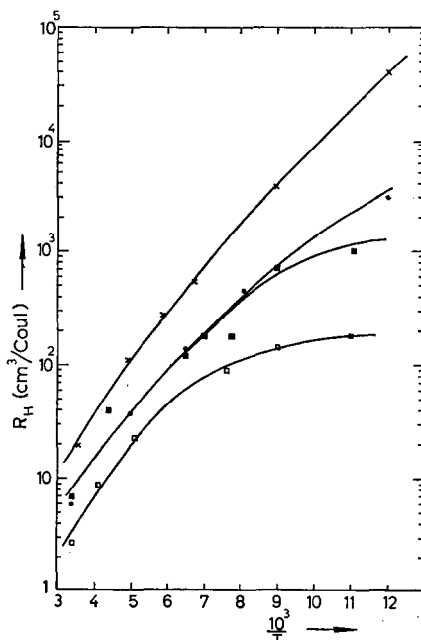


Fig. 1. Hall-coefficient of  $TiO_2$  samples doped with about 100 p.p.m.  $Al_2O_3$  and of various degrees of reduction ( $j \perp C$ ;  $H \parallel C$ ).

the National Lead Company. The mobility was found to equal that of undoped rutile. Hall-data are presented in fig. 1. It is seen that the transition from linear to bended

curves in the  $R_H$  vs  $1/T$  plot is now found at higher carrier concentrations than in undoped material <sup>5</sup>). These phenomena can be understood by a model with two different donor levels. At low reduction only the deeper levels remain filled as the shallow levels are exhausted by the compensating impurities.

We also performed measurements ( $\perp c$ -axis) of the thermopower of undoped reduced specimens having room temperature resistivities between  $10 \Omega \text{ cm}$  and  $2 \times 10^5 \Omega \text{ cm}$ . The results are plotted in fig. 2. In the region around  $300^\circ\text{K}$  the slopes of the curves are in reasonable agreement with those of the Hall-coefficients <sup>5</sup>). In very high resistance material the slope differs from that found at lower resistivity by about a factor 3. Compensation is probably important in this region. Below  $250^\circ\text{K}$  the thermopower decreases. Such behaviour may be found for polar scattering, due to a dependance of the transport contribution on temperature, cf. also measurements of Yahia and

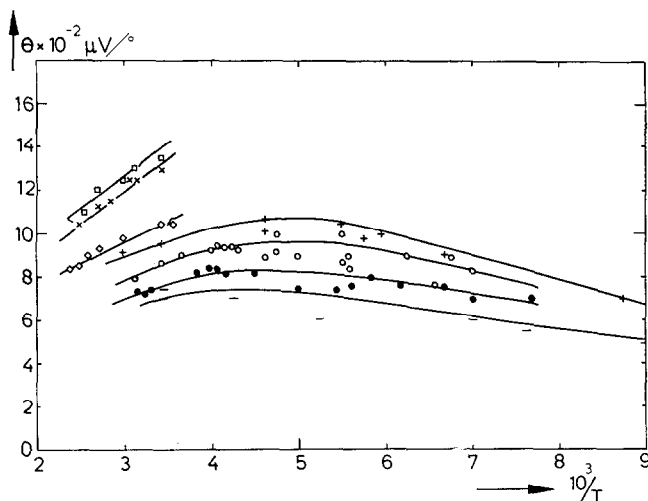


Fig. 2. Thermo-power of reduced pure rutile; temperature gradient  $\perp c$ -axis. Room temperature resistivities:

- |                                       |                                       |                                       |
|---------------------------------------|---------------------------------------|---------------------------------------|
| — $13 \Omega \text{ cm}$ .            | + $1 \times 10^3 \Omega \text{ cm}$ . | × $2 \times 10^5 \Omega \text{ cm}$ . |
| ● $28 \Omega \text{ cm}$ .            | ◇ $5 \times 10^3 \Omega \text{ cm}$ . | □ $1 \times 10^5 \Omega \text{ cm}$ . |
| ○ $2 \times 10^2 \Omega \text{ cm}$ . |                                       |                                       |

Frederikse on  $\text{Ti}_2\text{O}_3$  <sup>7</sup>). Neglecting the anisotropy and assuming the room temperature transport contribution to equal  $\frac{5}{2}(k/e)$ , effective masses of  $3\text{--}5 m_e$  corresponding to a density of states of  $1.2\text{--}3 \times 10^{20} \text{ cm}^{-3}$  were found, except for the  $13 \Omega \text{ cm}$  sample. These values are much lower than those previously reported <sup>1) 2)</sup>.

We also investigated the dependance of the conductivity on the electric field strength on specimens having room temperature resistivities of about  $10^3 \Omega \text{ cm}$ . A condensor was discharged across thin specimens by means of a thyatron. Capacitances of  $250 \text{ pF}$  and voltages up to  $10 \text{ kV}$  were used. The current - voltage characteristics were observed by means of an  $X\text{--}Y$  oscilloscope. Maximum field strengths were  $3\text{--}4 \times 10^5 \text{ V/cm}$  at room temperature and about  $3 \times 10^5 \text{ V/cm}$  at liquid air temperature both parallel and perpendicular to the  $c$ -axis. Chemical polishing in molten  $\text{KOH}$  appeared to be essential in order to avoid alinearities at the contacts. The observed characteristics remained linear even up to the high field strengths mentioned. If indeed masses of about  $30 m_e$  would be present the mobility at  $90^\circ\text{K}$  would correspond to a relaxation time of about  $3 \times 10^{-13} \text{ sec}$ . If this relaxation time is not reduced the energy

supplied to the electrons between two collisions would be at least 0.1 eV which is larger than the band width,  $E$ , if conservatively estimated to be  $3 \times 10^{-2}$  eV using  $E \cong \hbar^2/ma^2$  with  $a = 3 \times 10^{-8}$  cm. We feel that under these circumstances the current-field characteristics would show alinearities <sup>8)</sup> and that their absence should be another argument that the actual mass is markedly lower and so the band much wider.

It is doubtful whether the relaxation times following from our effective mass value still have their usual physical meaning as they are of the order of the reciprocal lattice frequency. Moreover, the polarization produced by the electron in the ionic lattice should be taken into account, the charge carrier being considered rather as a polaron than as an electron. Feynman *et al.*<sup>9)</sup> deduced a formula for the mobility based on a model by Fröhlich for temperatures much lower than the Debye temperature (670K<sup>o</sup>)<sup>1)</sup>.

$$\mu = \frac{e}{2m\omega\alpha} \left(\frac{w}{v}\right)^3 \exp\left(\frac{v^2 - w^2}{w^2 v}\right) \cdot \frac{3}{2} \frac{\exp z}{z}$$

$$z = \theta/T; m \cong 4m_e; \theta = \text{Debye temperature. } \alpha = \frac{1}{\sqrt{2}} \frac{e^2}{\bar{\epsilon}} \cdot \left(\frac{m}{\omega\hbar^3}\right)^{\frac{1}{2}}$$

$$\bar{\epsilon}^{-1} = -\epsilon_{\text{static}}^{-1} + \epsilon_{\text{opt.}}^{-1}. \quad \bar{\epsilon} \simeq 7 \quad \alpha \approx 5.$$

$$\omega = \frac{\hbar\theta}{\hbar} \approx 10^{14} \text{ sec}^{-1}.$$

$\omega$  denotes the angular frequency of the longitudinal phonon branch. For  $\alpha = 5$  the variational parameters  $v$  and  $w$  have the values 4.0 and 2.1 respectively <sup>9)</sup>.

The formula yields reasonable agreement with the average of the mobilities // and  $\perp$  the  $c$ -axis in the region between 100°K and 300°K. Below 100°K other scattering mechanisms may become important.

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