

**substance: hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>)**

**property: carrier concentration, electrical conductivity in pure Fe<sub>2</sub>O<sub>3</sub>**

**intrinsic carrier concentration**

$$n_i \quad 3.95 \cdot 10^{22} \exp(-1.8[\text{eV}]/2kT) \text{ cm}^{-3} \quad T \text{ in K} \quad 63\text{G}$$

The value of 1.8 eV is close to the reported indirect optical threshold [63G, 79K1]. The origin of this transition would in principle be  $\text{Fe}^{3+} + \text{Fe}^{3+} \rightarrow \text{Fe}^{4+} + \text{Fe}^{2+}$  or  $\text{Fe}^{3+} + \text{O}^{2-} \rightarrow \text{Fe}^{2+} + \text{O}^-$ . Cluster calculations support the first assignment [74T] whereas the optical data discussed below favours the second.

**conductivity**

Three distinct regions for air-fired samples are observed (Fig. 1, see also Fig. 3).

(A) Region of variable activation energy,  $T \leq 450^\circ\text{C}$ . Conductivity dominated by grain boundary resistance in polycrystalline samples, with  $E_A \approx 0.7$  eV. This region can be minimized by cooling under a reducing atmosphere. Grain boundary effects are clearly demonstrated by ac conductivity [51M].

(B) Region of low activation energy,  $450^\circ\text{C} \leq T \leq 800^\circ\text{C}$ ;  $E_A \approx 0.1$  eV. Ascribed to extrinsic conduction with "frozen-in" equilibrium.

parameters in the formula  $\sigma = n_d e A/T \exp(-\alpha/kT)$ :

$n_d$	$4.5 \cdot 10^{18} \text{ cm}^{-3}$	firing	$n_d$ : quenched donor concentration,	63G
$A$	$2270 \text{ cm}^2 \text{ K/Vs}$	temperature	$A$ : constant, $\alpha$ : activation	
$\alpha$	0.31 eV	$T = 1000^\circ\text{C}$	energy for electron mobility.	
$n_d$	$1.7 \cdot 10^{19} \text{ cm}^{-3}$	$T = 1100^\circ\text{C}$	Samples are ceramics.	
$A$	$207 \text{ cm}^2 \text{ K/Vs}$			
$\alpha$	0.22 eV			
$n_d$	$5.5 \cdot 10^{19} \text{ cm}^{-3}$	$T = 1200^\circ\text{C}$		
$A$	$44 \text{ cm}^2 \text{ K/Vs}$			
$\alpha$	0.13 eV			
$n_d$	$1.5 \cdot 10^{20} \text{ cm}^{-3}$	$T = 1300^\circ\text{C}$		
$A$	$42 \text{ cm}^2 \text{ K/Vs}$			
$\alpha$	0.12 eV			
$n_d$	$4 \cdot 10^{20} \text{ cm}^{-3}$	Fe <sub>2</sub> O <sub>3</sub>		
$A$	$232 \text{ cm}^2 \text{ K/Vs}$	+ 1.0 at% Ti		
$\alpha$	0.10 eV			

For unfired samples, containing no Fe<sup>2+</sup>, the region of low activation energy is far smaller, and the intrinsic region extends to much lower temperatures (Fig. 2) [63G].

Higher activation energies have been reported for this region: 0.39 eV [65G], 0.38 eV [48B]. Activation energy decreases strongly with Fe<sup>2+</sup> concentration [63G].

(C) Intrinsic region,  $T > 800^\circ\text{C}$ .

activation energies in region (C)

$E_A (= E_{g,th}/2)$	1.15 eV	all samples are ceramics	65G
	1.0 eV		63G
	1.17 eV		51M
	1.15 eV		71R
	1.06 eV		48B

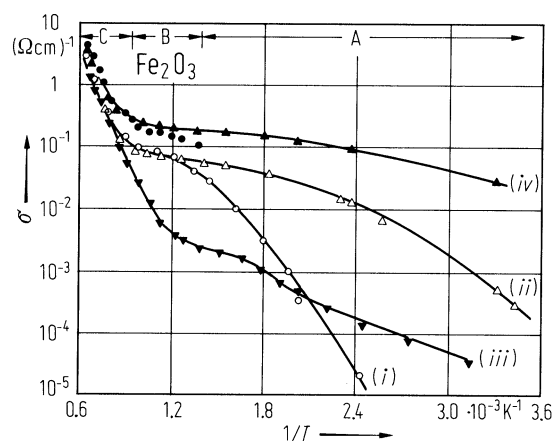
Resistance varies strongly with applied hydrostatic pressure; there is a collapse to a low-resistivity phase at  $\approx 440\text{...}520$  kbar [79K2].

## References:

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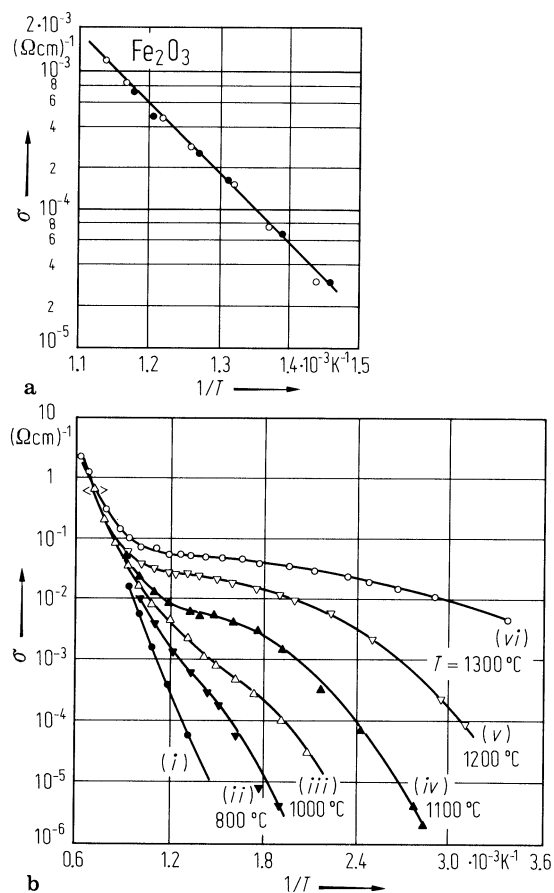
**Fig. 1.**

$\text{Fe}_2\text{O}_3$ . Conductivity vs. reciprocal temperature for high-purity samples (i) polycrystalline bar sintered at  $1300^\circ\text{C}$  in  $\text{O}_2$  and cooled to  $900^\circ\text{C}$  in ca. 30 min., (ii) polycrystalline bar sintered at  $1300^\circ\text{C}$  in  $\text{O}_2$  and quenched rapidly to  $20^\circ\text{C}$ , (iii) polycrystalline bar sintered at  $1300^\circ\text{C}$  and cooled slowly to RT, (iv) oxidized iron wire heated to  $1300^\circ\text{C}$  for 5 h and rapidly quenched to  $20^\circ\text{C}$ . A, B, C are the regions discussed in the tables. Solid circles: single crystal flux grown from sodium tetraborate; four-probe resistivity along the (111) plane of a specimen quenched after 13 h at  $1300^\circ\text{C}$  in air [63G].



**Fig. 2.**

$\text{Fe}_2\text{O}_3$ . (a) Conductivity vs. reciprocal temperature of an unfired compact between 400°C and 600°C, open circles: temperature rising, full circles: temperature falling; (b) influence of firing temperature on the conductivity of a compact sample, (i) unfired compact, (ii)-(vi) curves obtained for specimen quenched after 20 h at the stated temperatures [63G]. Ceramic samples.



**Fig. 3.**

$\text{Fe}_2\text{O}_3\text{:Mg}$ . Conductivity vs. reciprocal temperature for Mg doped ceramic samples fired at 1300°C. (1) pure sample, (2) 0.01 at% Mg, (3) 0.03 at% Mg, (4) 0.05 at% Mg, (5) 0.2 at% Mg [66G].

