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THE ELECTRICAL CONDUCTIVITY OF CHROMIUM TRIOXIDE AND ITS SUBOXIDES

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ABSTRACT

The electrical conductivity of CrO_3 and seven samples between CrO_3 and Cr_2O_3 is measured between room temperature and the temperature of preparation of the corresponding sample using an AC circuit. CrO_3 is found to be a semiconductor having a resistance of the order of 10^6 Ω when completely dried by heating to 100°C under a vacuum of 10^{-3} mm Hg. Cr_2O_3 gives a resistance of the order of 10^5–10^3 Ω in the temperature range 25–370°C. The samples in between possess values ranging between 10^5 and 10^4 Ω. The activation energies are interpreted as being due to the extrinsic range.

INTRODUCTION

Oxide systems of metals which exhibit variable valency are often complicated by the occurrence of nonstoichiometric compounds and the existance of more or less extensive regions of solid solutions. One of the more complex of such systems is that formed between oxygen and chromium as 3*d*. E ergy band calculation has been made for most of the elements but very little has been done for their compounds. Much of the band theory is based on measurements of transport properties, optical absorption, magnetic susceptibility, Hall effect, thermoelectric power, etc. The IR absorption of the oxides existing between CrO_3 and Cr_2O_3 has been studied previously [1] as an indicator of the possible presence of intermediate valencies in the samples. The electrical conductivity of the mother material CrO_3 has been studied [2] as an indicator of changes in a material, its transport properties and consequently its electron energy. A study of the nature of the oxides existing between CrO_3 and Cr_2O_3 was undertaken as part of a general study of the structures of the six-group transition element oxides and suboxides.

The electrical conductivity has been studied previously for the definite compositions CrO_3 [2–8], CrO_2 [9–15] and Cr_2O_3 [9,16–29]. The electrical conductivity of some oxides between CrO_3 and Cr_2O_3 has previously been studied to a small extent. Thus Cr_2O_5 was found by Kubota [9] to have high electrical conductivity. Also, Chapin et al. [30] determined the resistivity of

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hot pressed CrO_x ($1.89 < x > 2.03$) from 0–450°C. It could be seen that σ increased slightly with increasing temperature. Cojocaru et al. [31] studied the electrical conductivity of several samples between CrO_3 and Cr_2O_3 and determined the activation energy of each.

Extrapolating from what little is known, one can reinvestigate the electrical conductivity of the samples between CrO_3 and Cr_2O_3 to study the effect of temperature on, and the correlation between the electrical conductivity of the samples between CrO_3 and Cr_2O_3 to study the effect of temperature on, and the correlation between the electrical conductivity and the variation of the O/Cr ratio.

EXPERIMENTAL

Chromium trioxide (Merk) was used as starting material for preparing a series of oxides between CrO_3 and Cr_2O_3. Certain compositions were chosen to represent the stable steps or decomposition products of CrO_3 at different temperatures. The conditions followed for preparing and analysing the in between samples have been published elsewhere [1]. The prepared samples were $CrO_{2.988}$, $CrO_{2.71}$, $CrO_{2.41}$, $CrO_{2.399}$, $CrO_{2.3}$, $CrO_{1.66}$ and $CrO_{1.516}$.

The electrical conductivity was measured by applying the same technique described previously [32]. The resistance dispersion curves at different temperatures were established. A frequency of 20 kc s^{-1} was found to be suitable for obtaining the bulk resistance within the whole temperature range. The maximum temperature reached during measurements did not exceed the temperature of preparation of the samples in order to avoid any structure and composition modification.

RESULTS AND DISCUSSION

Figures 1–5 represent log σ vs. $1/T$ for all samples between CrO_3 and Cr_2O_3. Generally the curves fit the equation $\sigma = \sigma_0 \, e^{-\Delta E/KT}$ in certain regions of temperature. Since the electrical conductivity σ was measured using a high AC oscillation (20 kc s^{-1}) on polycrystalline samples the data obtained are due to the bulk property and not to the surface layers or grain boundaries.

For a disc of 1 cm diameter and with a thickness of about 0.3 cm it was found that CrO_3, when completely dried by heating to 100°C under vacuum of 10^{-3} mm Hg, gave a resistance of 10^6 Ω. Cr_2O_3 gave a resistance of the order 10^5–10^3 Ω in the range room temperature to 370°C. The samples in between ranged between 10^5 and 10^4 Ω.

Generally speaking all the curves showed an exhaustion region. The values of ΔE obtained from the linear parts are tabulated in Table 1. Some of these

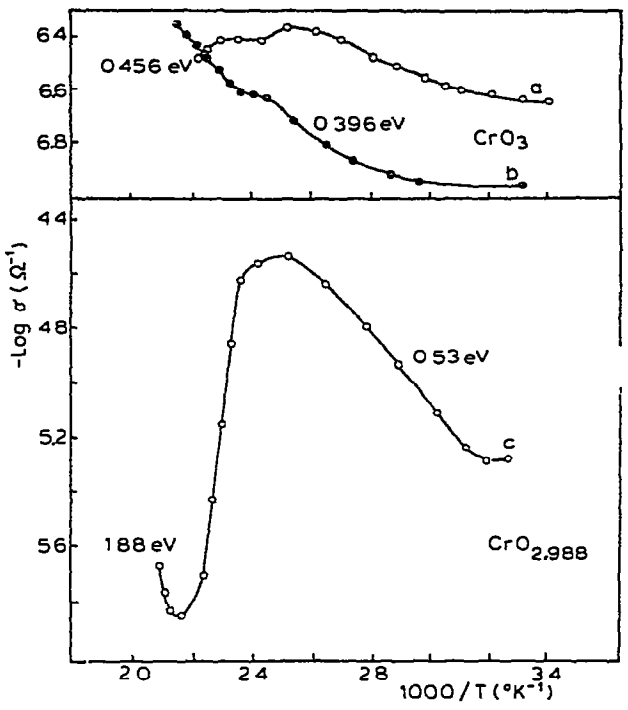

Fig 1. Variation of log σ vs $1/T$ for CrO_3 and $CrO_{2\,988}$.

values are reproducible in the higher temperature range regardless of previous history or heat treatment of the sample.

The experimental studies were hampered by a lack of information on the nature of the nonstoichiometry in CrO_3, the phase relationships in the chromium–oxygen system and also the gap width. Thus the obtained ΔE values in the temperature range may represent the gap width values which

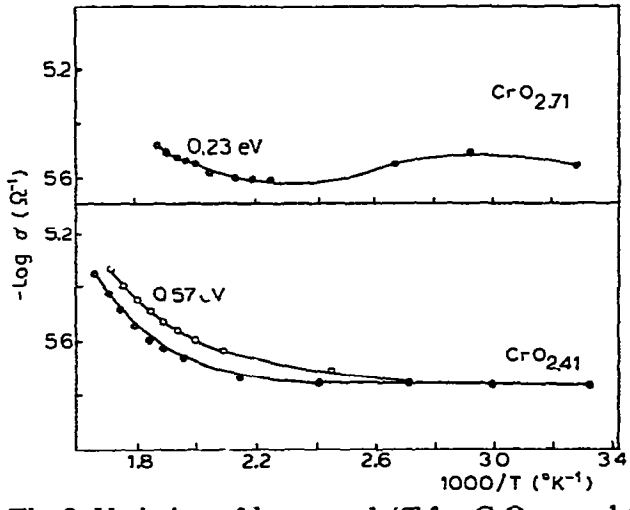

Fig. 2. Variation of log σ vs. $1/T$ for $CrO_{2\,71}$ and $CrO_{2\,41}$. ●, Heating; ○, cooling.

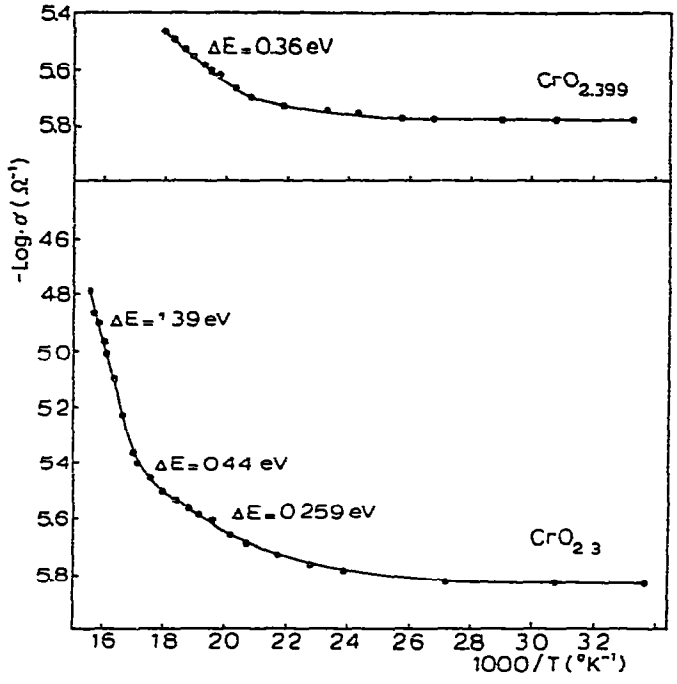

Fig. 3. Variation of log electrical conducvitity with $1/T$ for $CrO_{2\,399}$ and $CrO_{2\,3}$.

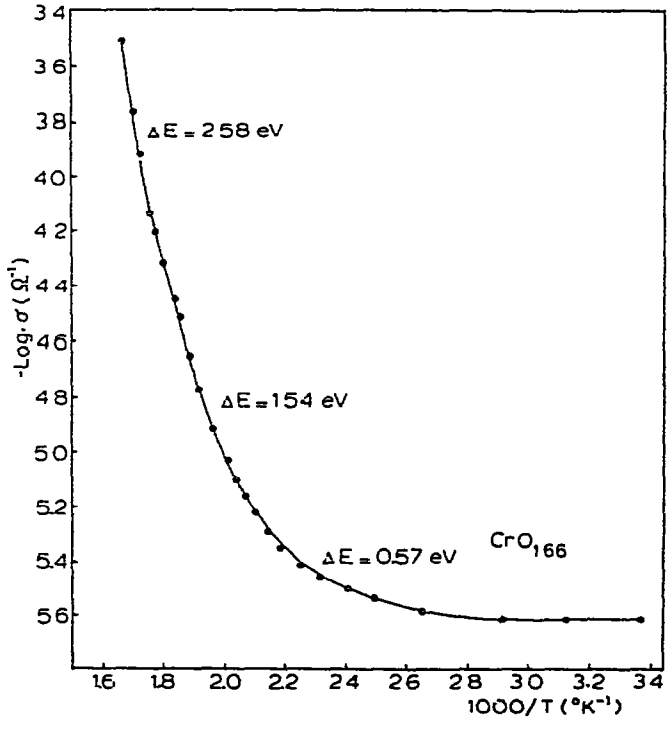

Fig. 4. Variation of log electrical conductivity with $1/T$ for $CrO_{1\,66}$.

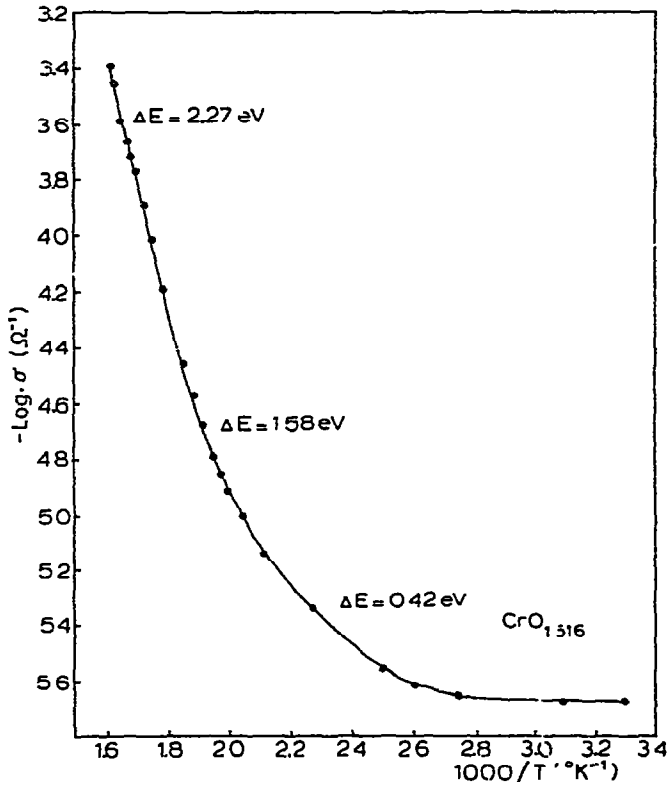

Fig. 5. Variation of log electrical conductivity with $1/T$ for $CrO_{1.516}$.

TABLE 1

Values of the activation energy for prepared chromium oxide samples

Sample	Activation energy (eV)		
	100°C	200–300°C	300°C
(1) CrO_3	0.4		
	0.456		
(2) $CrO_{2.988}$	0.53	1.88	
(3) $CrO_{2.71}$		0.23	
(4) $CrO_{2.41}$		0.57	
(5) $CrO_{2.399}$		0.36	
(6) $CrO_{2.3}$		0.259	1.394
		0.444	
(7) $CrO_{1.66}$		0.57	2.58
		1.54	
(8) $CrO_{1.516}$		0.42	2.27
		1.58	

will be later confirmed by optical means.

From the previous study on CrO_3 [2], it was concluded that CrO_3 exhibits a typical semiconducting behaviour which is attributed to the electron hopping from site to site. In Fig. 1 (curve c), sample 2 still preserves the behaviour of the highly hygroscopic Cr^{6+}. The effect of water present overcame that of the sample till reaching about 180°C where the conductivity began to increase with temperature giving a ΔE value of 1.88 eV.

Figures 2–5 represent the conductivity behaviour of samples 3–8. Samples 3, 4 and 5 showed a slight variation of conductivity with temperature. As is clear from the IR spectra [1], more than one valency of Cr is present, so there is wide exhaustion range. Samples 6–8 showed wide variation of conductivity with temperature with a change in the slope during the whole run. The last three samples changed the slope at two regions of temperature, 210–230°C and 290–304°C.

The cooling run for all samples coincided on the heating run except for sample 4 ($CrO_{2.41}$) where a hysteresis loop was observed (Fig. 2). This oxide was stated by Hirota and Kubota [33] to be antiferromagnetic.

The values of the conductivity at certain specific temperatures were drawn against the O/Cr ratio (Fig. 6). From Fig. 6 it is clear how the values change very widely with the O/Cr ratio, but the curves obtained at definite temperatures may be considered to be parallel i.e. the conductivity values for the different samples follow the same behaviour; this reflects specific behaviour for the different samples. Thus, as the O/Cr ratio decreases the

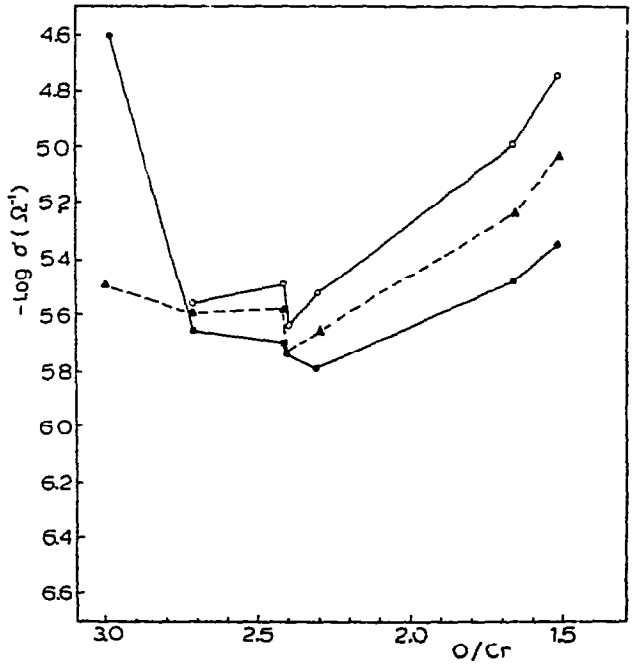

Fig. 6. Variation of log electrical conductivity with O/Cr ratio at ●, 150°C; ▲, 200°C; ○, 227°C

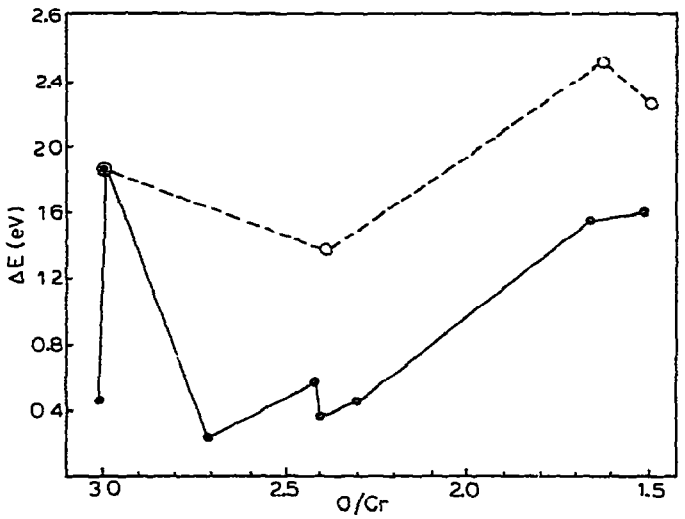

Fig. 7. Variation of the activation energy with the O/Cr ratio.

electrical conductivity value decreases, especially for intermediate samples (around $O/Cr = 2$), then it increases again for samples 7 and 8 which are closer to Cr_2O_3 [9]. This may indicate that the mechanism of conduction is not the same for all samples. It was found by Cojocaru et al. [31] that Cr_2O_3 was a *P*-type semiconductor while all higher oxides were of *n*-type.

Intermediate samples 3, 4, 5 and 6 have a different conduction mechanism. This may be due to the presence of more than one valency which may affect the transfer of electrons between the different valence cations. Returning to the activation energy values for the temperature range which is available for all samples (200–300°C), if these are drawn against the O/Cr ratio, Fig. 7 is obtained. This Fig. runs parallel with Fig. 6 for the variation of electrical conductivity at certain temperatures with the O/Cr ratio. This may be significant for the role of current carriers.

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