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EFFECT OF INCORPORATION OF SODIUM INTO COPPER(II) OXIDE

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Copper(II) oxide containing different amounts of sodium has been prepared. Thermoanalytical studies reveal differences in behaviour between sodium-incorporated samples and the control sample. A strong esr signal with $g = 2.1$ is explained by assuming a square planar configuration around the Cu^{2+} ion. The spin concentration is found to vary linearly with the sodium content, each sodium decoupling the spins of 40 Cu^{2+} ions in CuO. The signal is found to be present even in a reduced sample. The origin of such species is explained on the basis of antiferromagnetic decoupling of spins.

This paper deals with thermal and esr studies on copper(II) oxide containing a small percentage of sodium.

Basic carbonates were precipitated from copper(II) nitrate with sodium carbonate, and the sodium content of the samples was varied by washing with distilled water. A sodium-free control sample was prepared by using ammonium carbonate. The precipitates were dried at 120° for 12 hours. The particulars of the samples are given in Table 1.

The TG curve shows that the control sample A_1 is decomposed in a single step at 300° [1]. Analysis of the evolved gases confirms the evolution of H_2O and CO_2

Table 1

Method of preparation	Na in the oxide, %	Heated to		
		120 °C for 12 hours	400 °C for 2 hours	650 °C for 2 hours
Ppt with $(NH_4)_2CO_3$	Nil	A_1	A_2	A_3
Ppt with Na_2CO_3	0.32	B_1	B_2	B_3
-do-	0.25	C_1	C_2	C_3
-do-	0.20	D_1	D_2	D_3
-do-	0.16	E_1	E_2	E_3
-do-	0.12	F_1	F_2	F_3

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at this temperature. The samples containing sodium decomposed in two steps, at around 325° and 425° (Fig. 1). The decomposition at 325° was accompanied by the evolution of CO_2 and H_2O, while only H_2O was evolved at 425°.

The DTA curve of sample A_I (Fig. 1) showed one endothermic peak at around 300°, corresponding to the weight loss step in the TG curve. Other samples exhibited a similar endothermic peak around 325°. This peak was followed by another slow loss in weight around 425° as revealed by the broad endothermic peak, after which no enthalpy change could be detected up to 700°.

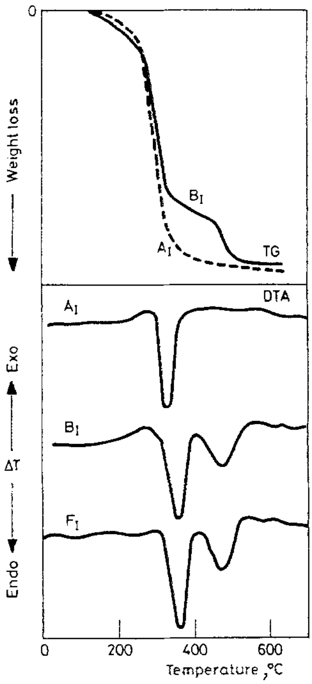

Fig. 1. TG and DTA curves of representative samples A_I — Sodium free sample. B_I, F_I — Sodium doped samples

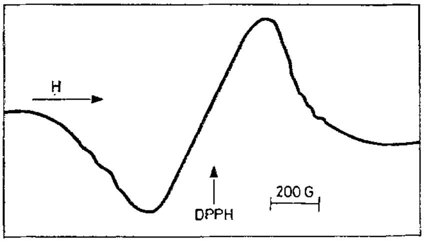

Fig. 2. Esr spectrum of sodium doped sample heated to 650 °C

The X-ray diffraction pattern of A_1 showed that it consisted of basic carbonate, while A_3 was the decomposition product CuO. In all samples containing sodium, although the main constituents were found to be similar, a few unidentified lines were found to be present.

Strong, symmetric, featureless spectra were observed for B_3, C_3, D_3, E_3 and F_3, as shown in Fig. 2. For others no signal was observed. The various parameters of the spectra are given in Table 2.

Table 2

Sample	*g*-values	Spins per *g*
B_3	2.097	3.4×10^{21}
C_3	2.112	2.6×10^{21}
D_3	2.119	2.1×10^{21}
E_3	2.124	1.9×10^{21}
F_3	2.123	1.2×10^{21}

Temperature variation of line-width	
Temp., °C	H_{pp}, in gauss
−150	1980
20	600
250	350

The variation of the spin concentration with the concentration of sodium is plotted in Fig. 3. The waterleached samples did not differ appreciably from the unleached one. This was expected, as no sodium was detected in the leaching water.

The signal remained unaltered on evacuation of the samples either at room temperature or at elevated temperatures (250°). The line width was found to vary considerably with temperature; the values are included in Table 2. The line shape did not change with variation of the sodium concentration. Neither in-situ nor external reduction caused any change in spectral pattern or intensity for samples B_3, C_3, D_3, E_3 and F_3.

Reduction studies on some representative samples with a spring-balance are illustrated in Fig. 4. The weight loss due to reduction in hydrogen atmospere is around 20.1% for all the samples. This shows that all the samples are completely reduced by hydrogen.

The thermal studies on the samples in air demonstrate the enhanced stability on doping with sodium. In the initial stage, it was evident that sodium had not penetrated the basic carbonate lattice, as it could easily be leached out. During heat treatment the initial lattice broke down in stages and the sodium gradually diffused in the host, till on prolonged heating at 650° the whole of the sodium had been incorporated in the CuO and leaching became difficult. The increased stability is manifested in the shift of the decomposition temperature towards higher values and in the retention of a hydrated phase of copper oxide.

Now CuO is antiferromagnetic and at room temperature no esr signal is expected, as observed in control samples A_2 and A_3 [2].

The intensities of the esr signals observed in the cases of B_3, C_3, D_3, E_3 and F_3 are very strong (for B_3 it is about 50% of the total copper); this does not favour its assignement due to isolated ions [3–7], which constitute only a small fraction of the total copper content [8]. For the same reason, as well as due to its stability at higher temperatures, formation of Cu^{3+} sites is also ruled out [9]. Hence, the probable reason for the appearance of the signal might be that sodium ions enter interstitial positions of the CuO lattice on heating at 650°. This produces lattice distortion and decouples the antiferromagnetically coupled spins of the neighbouring Cu^{2+} ions [10, 11]. From Fig. 5 it is seen that each sodium decouples the antiparallel spin ordering of 40 Cu^{2+} ions in these samples. With the reduction of exchange interaction the observed g values at room temperature correspond to the reported values for Cu^{2+} ions with square planar configuration [12]. A large degree of exchange interaction still persists, as evidenced by the sharp dependence of the esr line width upon temperature, but it is not sufficient to establish complete spin ordering in this group.

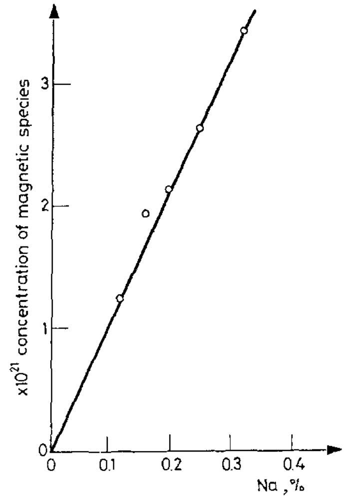

Fig. 3. Variation of spin concentration of the sodium doped samples heated to 650 °C with sodium content

Neither the esr signal intensity nor the spectral pattern were changed after reduction of samples (B_3, C_3, D_3, and F_3) at 220° and 400°. However, after reduction detuning of the cavity due to loss of microwave power arising from the eddy currents shows that an appreciable metallic state has been formed.

Thus, the question arises as to whether the species giving rise to the esr signal are in the reduced or unreduced state. An assessment of the extent of reduction shows that samples B_3, D_3 and D_2 are all completely reducible by hydrogen. Further confirmation of this is obtained from the X-ray studies on the reduced samples. Except for a minor constituent of the Cu^{1+} state, due to oxidation in air, all the reduced samples contain metallic copper phase only. Normally, delocalization or the unpaired electrons in the conduction band leads to diamagnetic metallic copper and no esr spectrum is expected. However, incorporation of sodium ions either in the oxide lattice or in the metallic copper makes them magnetic. In the CuO lattice, the presence of sodium ions perturbs the antiparallel spin alignment of neighbouring Cu^{2+} ions and thus an esr signal appears. In the reduced state, sodium ions might form grain boundaries for metallic copper and encapsulate the copper grains, so that formation of a conduction band is not favoured. In sodium-doped copper, therefore the unpaired electrons can not delocalize in the conduction band and the sample behaves as a magnetic material.

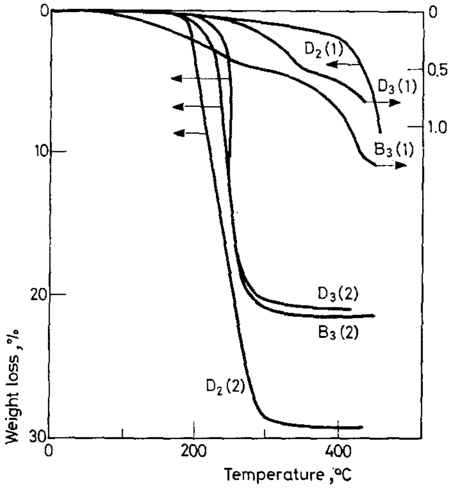

Fig. 4. Weight loss in spring balance of sodium doped samples. Curves 1 show the weight loss in air and curves 2 that in hydrogen. D_2 — sample initially heated to 400 °C, B_3, D_3 — samples heated to 650 °C

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