THERMAL EMF OF CuO AND ITS DEPENDENCE ON THE OXYGEN PARTIAL PRESSURE

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Because of the high sensitivity of the thermal emf \( \alpha \) to an extremely slight amount of superstoichiometric impurity \( \left( O_2 \right) \) in oxides of varying composition (amounts sometimes below the sensitivity limit of chemical analysis), thermoelectric effects can be studied as a function of the composition of a substance.

We report here an attempt to measure \( \alpha \) for CuO in various gaseous media over both moderate and high temperatures; such a study imposes special requirements on the experimental apparatus.

The desired oxygen pressure in the gas blown through the apparatus \( (P_{O_2} = 1-760 \text{ torr}) \) was achieved by the procedure described in [1]. Both the temperature and oxygen pressure were adjusted in a manner consistent with the stability range of CuO [2]. The temperature was measured within \( \pm 0.5^\circ \text{C} \) with a temperature gradient \( (\Delta T) \) of 30°. The error in the \( \alpha \) determination did not exceed 1.6%.

The CuO samples were synthesized by the procedure of [3]. During the measurements, the samples were held in the apparatus until a steady-state value of \( \alpha \) was established for the given \( \Delta T \). This procedure allowed us to achieve an equilibrium in CuO. In view of the reproducibility of our results, we conclude that this procedure was completely satisfactory.

Figure 1 shows the results of our measurements of the thermal emf of CuO and its temperature dependence for various values of \( P_{O_2} \) (curves 1-3). The first result which we see is that the sign of the thermal emf of CuO is the same in all cases, corresponding to p-type conductivity. In [4], however, CuO was stated to be an n-type semiconductor without a reference.

The value of \( \alpha \) increases as the stoichiometric CuO composition is approached; relatively large values of \( P_{O_2} \) correspond to relatively low magnitudes of \( \alpha \) for CuO. As Fig. 1 shows, curves 1 and 3 differ in the magnitude of \( \alpha \) by more than 325 \( \mu /\text{deg} \) as \( P_{O_2} \) changes by about three orders of magnitude (from 0.5 torr for curve 1 to 0.76 \( \cdot 10^3 \) torr for curve 3). Under the same conditions, however, the change in \( \alpha \) for \( Cu_2O \) is only 100 \( \mu /\text{deg} \) [5]. A sharper dependence of the isobar
\[
\alpha = \frac{1}{(f/T)}
\]
for CuO than for \( Cu_2O \) is consistent with the properties of these phases in the state diagram for the CuO -\( Cu_2O \) system [3] and is supported by the position of the isotherms
\[
\alpha = f\left(1/\frac{P_{O_2}}{p_{O_2}}\right).
\]
shown for comparison in Fig. 2. We see from Fig. 2 that at a given temperature \( \alpha \) remains a function of \( 1/\frac{P_{O_2}}{p_{O_2}} \). For example, as \( P_{O_2} \) changes by an order of magnitude, the value of \( \alpha \) for CuO may change by an amount roughly six times as much as for \( Cu_2O \).

The value \( \alpha \) does not always display the same high sensitivity to a superstoichiometric \( O_2 \) impurity in CuO; the sensitivity also varies in different manners for the phases which differ in stability (CuO, \( Cu_2O \)) in different ranges of the thermodynamic parameters \( (P_{O_2}, T) \). For example, the clearly-defined minimum of \( \alpha \) for CuO (point B in Fig. 1) is defined more clearly at low values of \( P_{O_2} \) (curve 1 in Fig. 1) and becomes noticeably less pronounced toward higher oxygen pressures (curve 3 in Fig. 1); this minimum coincides with the beginning of the active interaction of CuO with both impurity oxygen and with oxygen in the surrounding medium.
As the temperature is increased, the reduction of $\alpha$ (region AB in Fig. 1) predicted theoretically [6, 7] continues into the impurity-conductivity region only as long as the hardened state of CuO is retained [8]. This agreement between theory [6, 7] and experiment is also observed in the intrinsic-conductivity region of CuO (region CD in Fig. 1). However, in the region of the transition from impurity to intrinsic conductivity under certain thermodynamic conditions ($p_{O_2}$, T), CuO displays, in contradiction of the theory [6, 7], a direct dependence of $\alpha$ on the temperature (1) (region BC in Fig. 1). This anomalous behavior in dependence (1) has also been observed for V$_2$O$_5$ [9], Cu$_2$O$_3$ [10], TiO$_2$, and CdO [11]; the reason for this behavior has not yet been found. In this connection it is interesting to note that experimentally [3, 8] as the temperature is reduced, the mobility as well as the solubility of O$_2$ in the CuO lattice decreases. If the cooling occurs quite rapidly, the oxygen precipitated from CuO, which has a relatively low mobility, cannot escape from the oxide lattice in the gaseous phase. It is frozen, forming an impurity atmosphere. During the inverse process, as the temperature is raised, the role of the impurity atmosphere in the CuO characteristically changes in different manner in different temperature ranges. For example, below $\sim$390°C (region AB in Fig. 1), CuO is in a thermodynamically nonequilibrium (hardened) state [8], within which the behavior of $\alpha$ as a function of 1/T is that predicted by theory [6, 7]. Above 390°C (region BC in Fig. 1), however, the constancy of the CuO composition characteristic of the hardened state disappears [8]. The diffusion which occurs in the CuO is consistent with thermodynamic considerations: since the oxygen solubility in copper increases with increasing temperature, while its concentration falls (e.g., for CuO at $\sim$390°C [8]) below its limiting solubility, the impurity oxygen in CuO dissolves with increasing temperature. As a result, the impurity atmosphere in the lattice becomes much less important, thereby reducing the concentration of impurity current carriers, which in turn seems to be responsible for the increase in $\alpha$ with increasing temperature (region BC in Fig. 1).

Accordingly, at temperatures above those corresponding to the hardened state (in the impurity-conductivity region for CuO), the $\alpha$ (1/T) dependence corresponding to the theory [6, 7] is masked by an accompanying change in the composition (CuO); the sign of $\alpha$ for CuO also changes in different manners in different temperature ranges on the Cu–O$_2$ state diagram under certain thermodynamic conditions. For example, the minima of dependence (1) shift slightly toward higher temperatures for curves 3 and 2 (Fig. 1), which correspond to higher values of $p_{O_2}$. Noteworthy in this connection is the fact that the dissolution of impurity oxygen in CuO does not affect the weight of the CuO sample, so this effect cannot be detected by thermogravimetric measurements. However, the high sensitivity of thermoelectric measurements allow the anomalous $\alpha$ (1/T) dependence to be detected and thus allow a determination of the temperature at which the oxide of varying composition converts from the hardened state; finally, these measurements give information about the composition changes in such an oxide.

The slightly anomalous $\alpha$ (1/T) behavior in region AB (point L in Fig. 1), observed on all three curves (1–3), can apparently be studied in detail in a narrow temperature range by this highly sensitive method.