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Gibbs energy of formation of $Cu_2Ln_2O_5$ (Ln = Yb, Tm, Er, Ho, Dy) and $CuGd_2O_4$ compounds by the e.m.f. method

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Employing electrochemical cells with the solid zirconia electrolyte

$$Cu_2O, Cu_2Ln_2O_5, Ln_2O_3 \parallel O^{2-} \parallel \text{air}$$

and

$$Cu_2O, CuGd_2O_4, Gd_2O_3 \parallel O^{2-} \parallel \text{air}$$

the Gibbs free energy of formation of the solid $Cu_2Ln_2O_5$ (Ln=Yb, Tm, Er, Ho, Dy) and $CuGd_2O_4$ phases was determined. The results obtained were used to derive Gibbs free energy change of reactions of formation of these compounds from the respective oxides in the following form

$$\Delta G^0_{\text{oxides}}(Cu_2Yb_2O_5) = 19\,429 - 22.02T \text{ J mol}^{-1}$$

$$\Delta G^0_{\text{oxides}}(Cu_2Tm_2O_5) = 35\,275 - 34.09T \text{ J mol}^{-1}$$

$$\Delta G^0_{\text{oxides}}(Cu_2Er_2O_5) = 17\,427 - 19.61T \text{ J mol}^{-1}$$

$$\Delta G^0_{\text{oxides}}(Cu_2Ho_2O_5) = 18\,165 - 19.49T \text{ J mol}^{-1}$$

$$\Delta G^0_{\text{oxides}}(Cu_2Dy_2O_5) = 16\,648 - 17.58T \text{ J mol}^{-1}$$

$$\Delta G^0_{\text{oxides}}(CuGd_2O_4) = 9562 - 12.29T \text{ J mol}^{-1}$$

1. Introduction

Owing to the discovery of superconducting oxides, the properties of double oxide phases in the systems Ln–Cu–O (Ln = lanthanide) have also become of interest. The first systematic investigations of thermodynamic properties of these compounds were carried out by Tretyakov *et al.* [1]. Later, Petrov *et al.* [2] took into account the formation of $CuLnO_2$ phases in those systems, and measured the free energy of formation of the compounds with Ln = La, Pr, Nd, Sm and Eu. Recently, in a series of papers Jacob and co-workers reinvestigated systems with gadolinium [3], thulium and lutetium [4], holmium [5], and terbium, dysprosium, erbium and ytterbium [6].

In the previous paper we reported results of our investigations on the Gibbs free energy of formation of $Cu_2Lu_2O_5$ [7]. In the present study, Gibbs free energy of formation of $Cu_2Ln_2O_5$ (where Ln = Yb, Tm, Er, Ho, and Dy) and $CuGd_2O_4$ was determined.

2. Experimental procedure

2.1. Materials

Copper oxide, CuO (99.99%), was obtained from Johnson and Matthey. Ytterbium and dysprosium oxides (Yb_2O_3 and Dy_2O_3) were 99.9% pure and were both obtained from Unocal, Molycorp Inc., USA. Holmium oxide (Ho_2O_3) was 99.9% pure and was obtained from Apache Chemicals Inc., USA while thulium oxide (Tm_2O_3) of the same purity was from Johnson and Matthey, Germany. Erbium oxide (Er_2O_3) was 99.99% pure and was obtained from Rhone Poulenc, France. Double oxides were all synthesized in a similar manner by heating pressed pellets containing a proper mixture of CuO and Ln_2O_3 (Ln = Yb, Tm, Er, Ho, Dy, Gd) under a stream of dry oxygen at 1223 K for 48 h with one intermediate grinding and pelletizing after 24 h. Prepared compounds were used in the preparation of working electrodes for respective electrochemical cells. Fully stabilized zirconia tubes, closed at one end (diameter 8 mm), were supplied by the Friedrichsfeld GmbH, Germany.

2.2. Procedure

The electrochemical cells of the type

$$Cu_2O + Ln_2O_3 + Cu_2Ln_2O_5 \parallel O^{2-} \parallel \text{air} \qquad \text{(Ia)}$$

and

$$Cu_2O + Gd_2O_3 + CuGd_2O_4 \parallel O^{2-} \parallel \text{air} \qquad \text{(Ib)}$$

(where Ln = Yb, Tm, Er, Ho, Dy) were assembled to measure oxygen potential over coexisting phases. The cell construction and experimental procedure were essentially identical to that described in the previous paper concerned with the thermodynamic stability of $Cu_2Lu_2O_5$ phase [7]. Because the oxygen potential over the working electrode is related to the measured e.m.f. by the relationship

$$E_{I_{a,b}} = (RT/4F)\ln(0.21/p_{O_2}) \qquad (1)$$

the Gibbs free energy change of the reactions which establish the equilibrium oxygen pressure over the respective working electrodes

$$Cu_2O + 1/2O_2 + Ln_2O_3 = Cu_2Ln_2O_5 \qquad (2)$$

(Ln = Yb, Tm, Er, Ho, Dy), and

$$Cu_2O + 1/2O_2 + 2Gd_2O_3 = 2\,CuGd_2O_4 \qquad (3)$$

were calculated from equilibrium constants $K_{(2)}$ and $K_{(3)}$ (defined as $1/(p_{O_2})^{1/2}$). Equilibrium oxygen pressure was derived from measured e.m.fs using Equation 1. Next, combining either Reaction 2 or Reaction 3 with the reaction

$$2\,CuO = Cu_2O + 1/2O_2 \qquad (4)$$

the Gibbs free energy of formation of respective double oxides from component oxides

$$2\,CuO + Ln_2O_3 = Cu_2Ln_2O_5 \qquad (5)$$

(Ln = Yb, Tm, Er, Ho, Dy), and

$$CuO + Gd_2O_3 = CuGd_2O_4$$

was obtained.

3. Results

Electromotive force values measured for cells Ia and b with different working electrodes as a function of temperature are shown in Fig. 1a–f.

Linear dependencies of e.m.f. versus temperature, obtained by the least-squares method, are represented by the equations given in Table I.

The respective ΔG^0_T equations calculated for Reactions 2 and 3 from obtained e.m.fs are also given in this table. Finally, using Gibbs free energy change determined for Reaction 4 in our previous work [7], the respective Gibbs free energy change for the formation of solid phases according to Reaction 5 was obtained. Calculated quantities are compared in Table II with results of earlier studies, as well as with the heat of formation of respective phases from oxides measured by Takayama–Muromachi and Navrotsky [8] at 977 K with high-temperature solution calorimetry.

TABLE I Temperature dependence of e.m.fs and corresponding Gibbs free energy change for Reactions 2 and 3

$Ln \equiv$	E(mV) = $a + b\,T$		ΔG^0_T for Reactions 2 and 3 (J mol^{-1})	
Yb	576.7	$-0.4049T$	$\Delta G^0_{(2)} =$	$-111\,292 + 71.65T$
Tm	496.6	$-0.3424T$	$\Delta G^0_{(2)} =$	$-95\,446 + 59.58T$
Er	587.1	$-0.4174T$	$\Delta G^0_{(2)} =$	$-113\,293 + 74.06T$
Ho	583.3	$-0.4180T$	$\Delta G^0_{(2)} =$	$-112\,556 + 74.18T$
Dy	591.1	$-0.4279T$	$\Delta G^0_{(2)} =$	$-114\,073 + 76.09T$
Gd	578.3	$-0.3916T$	$\Delta G^0_{(3)} =$	$-111\,595 + 69.08T$

4. Discussion

The obtained results indicate that all compounds are entropy stabilized and become unstable below a certain characteristic temperature. It is also clear from Fig. 1 that this experimental temperature differs from the value calculated from the respective equations given in Table II. Measured e.m.fs reach the $CuO–Cu_2O$ line at the point which does not coincide with the extrapolation of the $E(T)$ equation, showing a kind of "transition range" with a different temperature dependence. No explanation of this behaviour can be given at present.

The formation of $CuLnO_2$-type compounds was not detected in the working electrodes after the experiments. This fact is compatible with earlier statements that $Cu_2Ln_2O_5$ phases are the only phases existing in the Cu–Ln–O systems under consideration. This is also true in the case of the Cu–Gd–O system. A recent study of Zhang and Osamura [9] showed that in the Cu–Gd–O system, only one compound $CuGd_2O_4$ exists. This conclusion was supported by Jacob *et al.* [3] who used an e.m.f. technique to determine the oxygen potential diagram for the Cu–Gd–O system. The observed differences (except for thulium compound) between our values and those reported by Tretyakov *et al.*, and Jacob and co-workers, result more from the data for $CuO–Cu_2O$ equilibrium accepted for calculations than from differences in measured e.m.fs. The influence of accepted data for the $CuO–Cu_2O$ equilibrium on the calculated Gibbs free energy of formation from the oxides was discussed in a previous paper [7]. However, a bigger difference is observed between ΔH^0_{oxide} values obtained from calorimetric measurements and those derived from measured e.m.fs. Though this difference is not surprising (because the heat of formation obtained from e.m.fs is very susceptible to the slope of the E versus T dependence) the calorimetric values

TABLE II Gibbs free energy change for reaction of formation from oxides

$Ln \equiv$	ΔG^0_{oxides} (J mol^{-1})						ΔH^0_{oxides} (J mol^{-1}) [8]
	This work		Tretyakov *et al.* [1]		Jacob *et al.* [3–6]		
Yb	19429	$-22.02T$	12428	$-16.60T$	9920	$-13.70T$	6400
Tm	35275	$-34.09T$	–	–	10400	$-14.0T$	-200
Er	17427	$-19.61T$	20264	$-21.74T$	10750	$-13.99T$	9700
Ho	18165	$-19.49T$	–	–	11190	$-13.8T$	7800
Dy	16648	$-17.58T$	15320	$-16.83T$	11480	$-13.51T$	9000
Gd	9562	$-12.29T$	8800	$-11.74T$	8230	$-11.2T$	-300

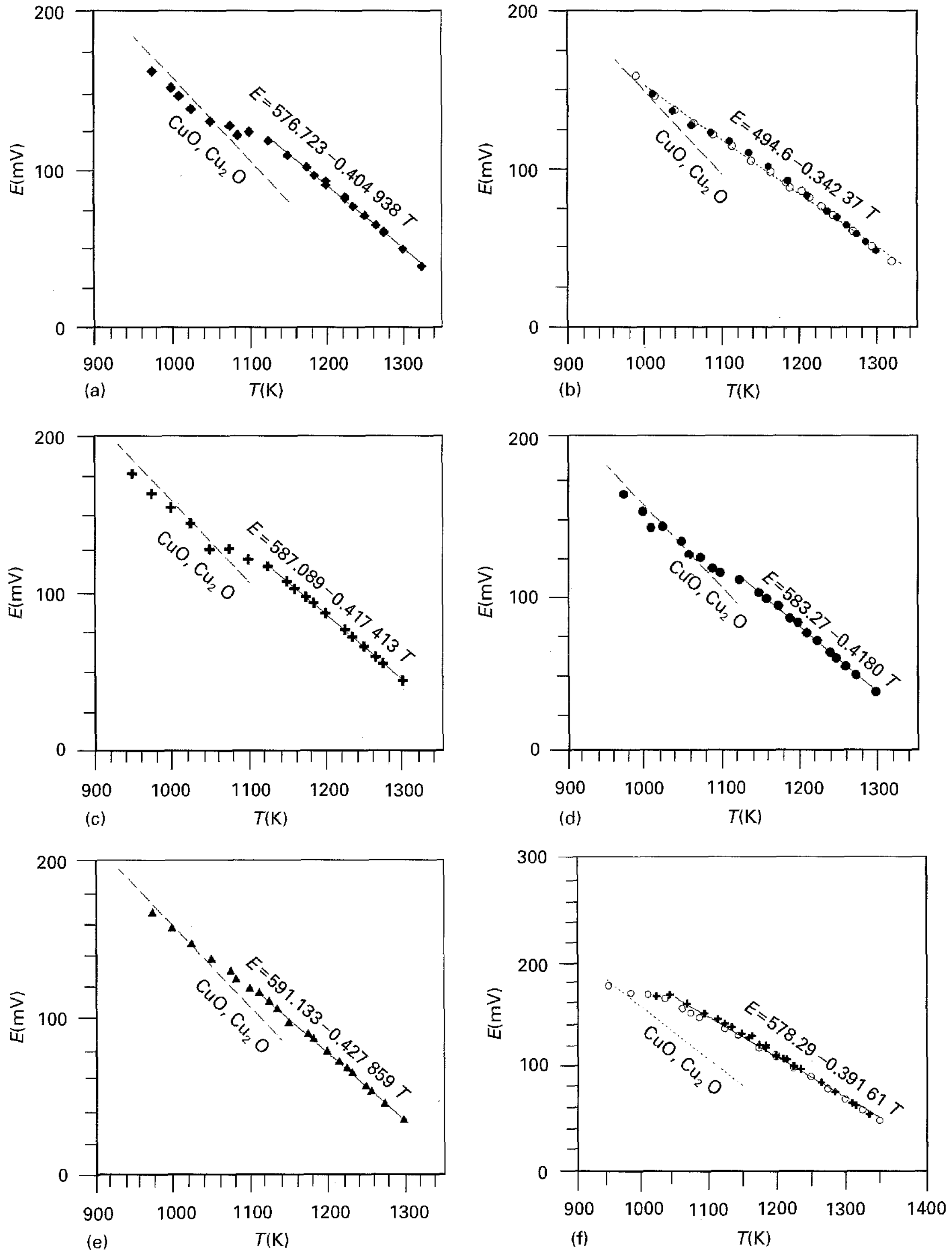

Figure 1 Variation of e.m.f. with temperature for respective electrochemical cells. (a) Cu_2O, Yb_2O_3, $Cu_2Yb_2O_5 \| O^{2-} \|$ air; (b) Cu_2O, Tm_2O_3, $Cu_2Tm_2O_5 \| O^{2-} \|$ air; (c) Cu_2O, Er_2O_3, $Cu_2Er_2O_5 \| O^{2-} \|$ air; (d) Cu_2O, Ho_2O_3, $Ho_2Cu_2O_5 \| O^{2-} \|$ air; (e) Cu_2O, Dy_2O_3, $Cu_2Dy_2O_5 \| O^{2-} \|$ air; (f) Cu_2O, Gd_2O_3, $CuGd_2O_4 \| O^{2-} \|$ air.

obtained for systems with thulium and gadolinium are difficult to explain.

On analysing interactions in the CuO–Ln_2O_3 systems Takayama-Muromachi and Navrotsky [8], pointed out that rare-earth cations bigger than Gd^{3+} can form $Cu_2Ln_2O_5$ phases, while for Gd^{3+} and smaller cations, transition into $CuLn_2O_4$ occurs. In these systems, $CuLnO_2$ phase also appears at low oxygen potential. It seems that gadolinium still behaves as other lanthanides from lutetium to dysprosium. However, for the next element, euxopium, the formation of $CuEuO_2$ compound during investigations of the ternary Cu–Eu–O system [2, 10] was observed. Thus, either gadolinium or euxopium seems to be the lanthanide which changes the trend of the phase compatibility relations in the Cu–*Ln*–O systems. One may anticipate that this change will influence tie-line locations in the CuO–BaO–Ln_2O_3 systems. Indeed, general trends in phase formation, solid-solution formation and phase relationships in these systems correlated with the ionic size of the lanthanides suggested by Wong-Ng *et al.* [11] support this point of view. However, more data on thermodynamic stability of the phases existing in those ternary systems are needed to understand observed changes in phase relations.

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