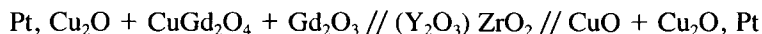


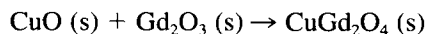
# Phase Relations in the System Cu-Gd-O and Gibbs Energy of Formation of CuGd<sub>2</sub>O<sub>4</sub>

K.T. JACOB, TOM MATHEWS, and J.P. HAJRA

The phase relations in the system Cu-Gd-O have been determined at 1273 K by X-ray diffraction, optical microscopy, and electron microprobe analysis of samples equilibrated in quartz ampules and in pure oxygen. Only one ternary compound, CuGd<sub>2</sub>O<sub>4</sub>, was found to be stable. The Gibbs free energy of formation of this compound has been measured using the solid-state cell

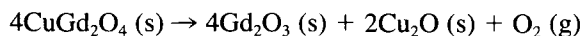


in the temperature range of 900 to 1350 K. For the formation of CuGd<sub>2</sub>O<sub>4</sub> from its binary component oxides,



$$\Delta G^\circ = 8230 - 11.2T (\pm 50) \text{ J mol}^{-1}$$

Since the formation is endothermic, CuGd<sub>2</sub>O<sub>4</sub> becomes thermodynamically unstable with respect to CuO and Gd<sub>2</sub>O<sub>3</sub> below 735 K. When the oxygen partial pressure over CuGd<sub>2</sub>O<sub>4</sub> is lowered, it decomposes according to the reaction



for which the equilibrium oxygen potential is given by

$$\Delta\mu_{\text{O}_2} = -227,970 + 143.2T (\pm 500) \text{ J mol}^{-1}$$

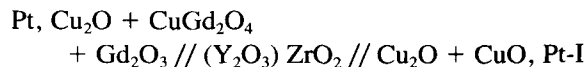
An oxygen potential diagram for the system Cu-Gd-O at 1273 K is presented.

## I. INTRODUCTION

THE thermodynamic properties of ternary phases in the Ln-Cu-O systems are of interest because they constitute one bounding face of the quaternary systems Cu-Ln-Ba-O containing the superconducting compounds LnBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-8</sub> (Ln = Y, Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm, and Yb),<sup>11-41</sup> Ln<sub>2</sub>Ba<sub>4</sub>Cu<sub>7</sub>O<sub>15-8</sub> (Ln = Y, Eu, Gd, Dy, Ho, Er and Yb),<sup>15,6,71</sup> and LnBa<sub>2</sub>Cu<sub>4</sub>O<sub>8</sub> (Ln = Y, Nd, Sm, Eu, Gd, Dy, Ho, Er, and Tm).<sup>18,91</sup> Several compounds have been reported in the Cu-Ln-O systems. The Ln<sup>3+</sup> oxides (Ln = La, Pr, Nd, Sm, Eu, and Gd) react with CuO to form CuLn<sub>2</sub>O<sub>4</sub>,<sup>10,11</sup> oxides of Ln = Tb, Dy, Ho, Er, Tm, Yb, Lu, and Y form compounds of the type Cu<sub>2</sub>Ln<sub>2</sub>O<sub>5</sub>.<sup>121</sup> A third type of compound CuLnO<sub>2</sub> with Ln = La, Pr, Nd, Sm, Eu, and Y has been reported<sup>13,141</sup> in which copper is monovalent. This phase is generally stable at low oxygen partial pressures under equilibrium conditions at high temperature. Cava *et al.*<sup>151</sup> have synthesized and characterized two new compounds, La<sub>2</sub>Cu<sub>2</sub>O<sub>5</sub> and La<sub>8</sub>Cu<sub>7</sub>O<sub>19</sub>. They appear to be stable only in very narrow temperature ranges in air and oxygen. Bringley *et al.*<sup>161</sup> have synthesized LaCuO<sub>3-8</sub> at high oxygen pressures.

As part of a larger research program on phase relations and thermodynamic properties of oxide systems containing superconducting compounds, the system Cu-Gd-O was investigated. Phase relations in the Cu-Y-O system

have been reported earlier by Kale and Jacob.<sup>171</sup> Tretyakov *et al.*<sup>181</sup> have measured the Gibbs energy of formation of CuGd<sub>2</sub>O<sub>4</sub> using a solid-state galvanic cell. Zhang and Osamura<sup>191</sup> have studied the decomposition of CuGd<sub>2</sub>O<sub>4</sub> and CuO as a function of oxygen partial pressure using a combined thermogravimetric and differential thermal analysis technique (TG-DTA). The Gibbs energy of formation of CuGd<sub>2</sub>O<sub>4</sub> was calculated from the decomposition temperatures. The entropy of formation of CuGd<sub>2</sub>O<sub>4</sub> from component oxides evaluated from the measurements of Zhang and Osamura<sup>191</sup> is opposite in sign to that obtained by Tretyakov *et al.*<sup>181</sup> Hence, the Cu-Gd-O system was reinvestigated. The phase relations in the ternary system Cu-Gd-O were first established. An electrochemical cell was then designed to measure the Gibbs energy of formation of CuGd<sub>2</sub>O<sub>4</sub>. A solid-state galvanic cell with the configuration



was used in the temperature range of 900 to 1350 K. From the thermodynamic data, an oxygen potential diagram for the Cu-Gd-O system is constructed at 1273 K.

## II. EXPERIMENTAL PROCEDURE

### A. Materials

The oxide starting materials used in the preparation of ternary compositions were fine powders of Cu<sub>2</sub>O, CuO, and Gd<sub>2</sub>O<sub>3</sub>, each of purity greater than 99.99 pct. The compound CuGd<sub>2</sub>O<sub>4</sub> was prepared by heating an intimate

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mixture of CuO and Gd<sub>2</sub>O<sub>3</sub> in the appropriate molar ratio at 1273 K for 90 ks in flowing oxygen. The product was identified by powder X-ray diffraction to be single-phase CuGd<sub>2</sub>O<sub>4</sub>. The metals Cu and Gd used in this study were of 99.99 pct purity. The argon gas, used to provide an inert blanket over the reference and measuring electrodes of the cell, was also 99.99 pct pure. It was further dried by passing over silica gel and anhydrous P<sub>2</sub>O<sub>5</sub> and deoxidized by passing over copper wool at 675 K. The yttria-stabilized zirconia solid electrolyte tube was obtained from a commercial source.

### B. Determination of the Phase Diagram

The phase relations in the ternary system Cu-Gd-O were explored by equilibrating mixtures containing metals and oxides at 1273 K for 500 ks, followed by quenching into liquid nitrogen and phase identification. The fine powders were mixed in an agate mortar, and the mixtures were pelletized in a steel die. The pellets, contained in alumina crucibles, were generally equilibrated inside quartz ampules sealed under vacuum or reduced pressure of argon gas. This is to prevent oxidation of the alloy and the lower oxides. The mixtures containing only oxides in their highest oxidation state were equilibrated under pure oxygen at a pressure of  $1.01 \times 10^5$  Pa. The apparatus used was similar to that described earlier.<sup>[20]</sup> At the end of the equilibration period, the samples were quenched in liquid nitrogen. The samples were examined under an optical microscope. The phases present in the equilibrated samples were identified by X-ray diffraction and electron microprobe analysis. The overall composition of the analyzed samples is shown in Figure 1.

### C. Emf Measurements Using (Y<sub>2</sub>O<sub>3</sub>) ZrO<sub>2</sub> Electrolyte

The experimental arrangement of cell I was similar to that used by Kale and Jacob.<sup>[17]</sup> The main feature of the cell design was the separation of the two electrode compartments using a long tube of stabilized zirconia, closed at one end. This was necessary because of the relatively high oxygen partial pressure at each electrode. Without the separation of electrode compartments, there would have been significant oxygen transport *via* the gas phase between the electrodes, resulting in nonsteady electromotive force (emf) readings. The apparatus was designed to minimize the free volume over the electrode compartments. The electrodes of cell I were initially flushed by two separate streams of argon gas. The argon flow was then cut off, and the electrodes were allowed to establish their own equilibrium oxygen partial pressure. Continued flushing with inert gas was found to result in loss of oxygen from the electrodes by entrainment, especially at high temperatures. The cell assembly was housed inside a vertical furnace such that the electrodes were maintained in the even temperature zone. A foil of stainless steel was wrapped around the outer alumina tube of the cell. The foil was grounded to minimize induced voltage on the platinum leads. The cell temperature was measured by a Pt/Pt-13 pct Rh thermocouple placed adjacent to the measuring electrode. The temperature of the cell was controlled within  $\pm 1$  K.

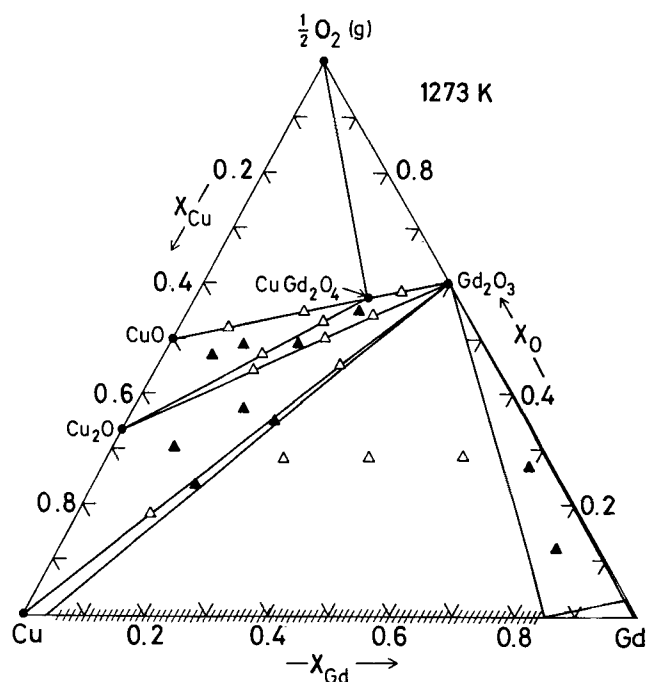


Fig. 1—The isothermal section of the ternary system Gd-Cu-O at 1273 K.

The reference electrode of cell I was prepared by compacting an intimate mixture of Cu<sub>2</sub>O and CuO in the molar ratio 1:2 inside the solid electrolyte tube with a platinum lead embedded in the mixture. The working electrode was prepared by ramming an intimate mixture of Cu<sub>2</sub>O, Gd<sub>2</sub>O<sub>3</sub>, and CuGd<sub>2</sub>O<sub>4</sub> in the molar ratio 1:1:2 against the closed end of an alumina tube with a platinum lead embedded in it. The solid electrolyte tube was spring loaded against the working electrode mixture.

The emf of the solid-state galvanic cell I was measured as a function of temperature in the range of 900 to 1350 K with a high impedance digital electrometer. The reversibility of the cell was checked by microcoulometric titration in both directions. During the titration, the oxygen potential at each electrode was displaced by an infinitesimal amount. The open circuit emf of the cell was followed after each titration, during which a current of  $\sim 100 \mu\text{A}$  was passed for 500 seconds. It was found that the emf returned to the steady value before the titration in each case in 1.5 to 2 ks. The cell emf was also found to be reproducible on temperature cycling. The phase composition of the electrodes was checked after each experiment by X-ray diffraction. The phases present in the electrodes were unaltered during the experiment.

## III. RESULTS AND DISCUSSION

### A. Phase Diagram

The phase relations in the Cu-Gd-O system at 1273 K obtained from the analysis of samples in this study and phase diagrams for the constituent binaries Cu-O and Cu-Gd available in the literature<sup>[21]</sup> are shown in Figure 1. Only one ternary compound, CuGd<sub>2</sub>O<sub>4</sub>, was

found to be stable at 1273 K. This compound does not appear to have a large nonstoichiometric range. The CuO content of  $\text{CuGd}_2\text{O}_4$  in equilibrium with  $\text{Gd}_2\text{O}_3$  was different from that in equilibrium with CuO by only 0.9 mole pct. The mutual solubility between  $\text{Gd}_2\text{O}_3$  and the oxides of copper as determined by microprobe analysis was also less than 0.8 mole pct. Both solid Cu and liquid Cu-Gd alloys were in equilibrium with  $\text{Gd}_2\text{O}_3$ .

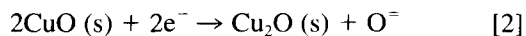
It is interesting that the compound  $\text{CuGdO}_2$  with copper in monovalent state does not exist, at least in the range of conditions encountered in this study. The  $\text{CuLnO}_2$  compound is reported to be stable for the lighter Ln elements up to and including Eu. Gadolinium is the first element in the rare earth series for which this compound is unstable. The destabilization of this  $\text{CuLnO}_2$  compound is linked to the smaller size of the heavier  $\text{Ln}^{3+}$  ions.

### B. Emf Measurements

The variation of the emf of galvanic cell I with temperature is shown in Figure 2. Within the experimental error, the emf is a linear function of temperature. The least-squares regression analysis gives

$$E_1 = -85.3 + 0.116T (\pm 0.5) \text{ mV} \quad [1]$$

The error limit corresponds to twice the standard deviation. The anodic reaction for cell I can be written as



The corresponding cathodic reaction is

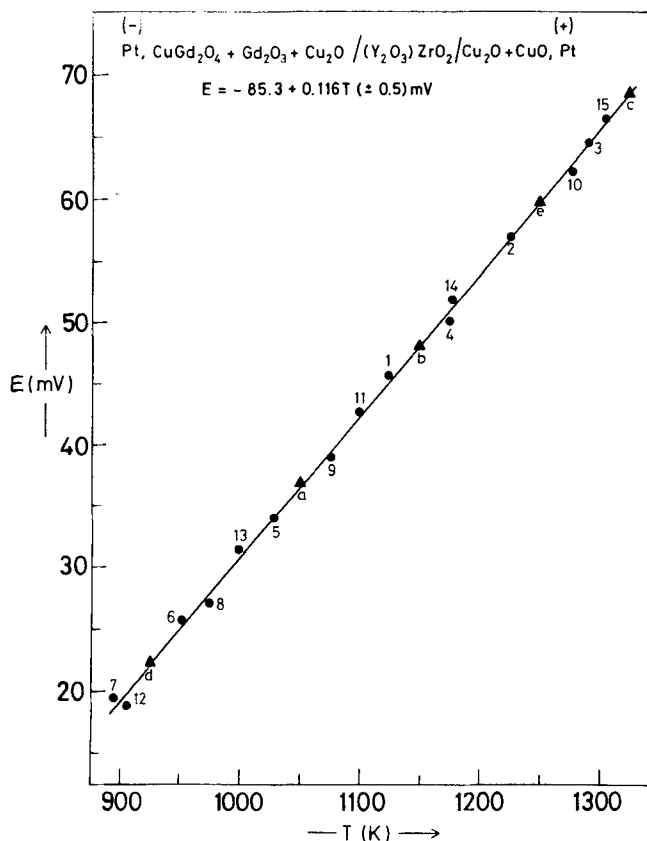
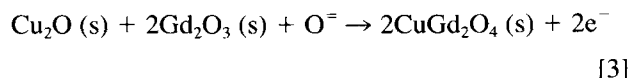
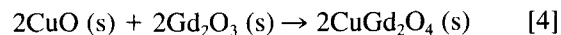


Fig. 2—The temperature dependence of the emf of cell I.



The virtual cell reaction can be represented as



From the measured emf, the Gibbs free energy change for Reaction [4] is obtained:

$$\Delta G_4^\circ = -nFE_1 = 16,460 - 22.4T (\pm 100) \text{ J mol}^{-1} \quad [5]$$

where  $n = 2$  is the number of electrons involved in the electrode reactions and  $F$  is the Faraday constant. The enthalpy of formation of  $\text{CuGd}_2\text{O}_4$  from its component oxides is positive. The compound is entropy stabilized at high temperature. It is thermodynamically unstable below 735 K with respect to CuO and  $\text{Gd}_2\text{O}_3$ .

The Gibbs free energy change for Reaction [4] is shown in Figure 3 as a function of temperature. The values obtained by Tretyakov *et al.*<sup>[18]</sup> and Zhang and Osamura<sup>[19]</sup> are also indicated for comparison. The Gibbs energy changes for the dissociation of  $\text{CuGd}_2\text{O}_4$  and CuO reported by Zhang and Osamura<sup>[19]</sup> were combined to obtain the free energy change corresponding to Reaction [4]. The data from Tretyakov *et al.*<sup>[18]</sup> were derived by combining the emf of two cells with  $\text{Cu}_2\text{O} + \text{Gd}_2\text{O}_3 + \text{CuGd}_2\text{O}_4$  and  $\text{Cu}_2\text{O} + \text{CuO}$  as the measuring electrodes and air as the reference. The results of this study are in excellent agreement with those of Tretyakov *et al.*<sup>[18]</sup> A similar technique was used in both of the studies, the only difference being the use of air reference electrode by Tretyakov *et al.*<sup>[18]</sup> Strictly, one has to apply corrections for atmospheric pressure and humidity variations, when air is used as a reference electrode in galvanic cells. Factors other than altitude have a significant

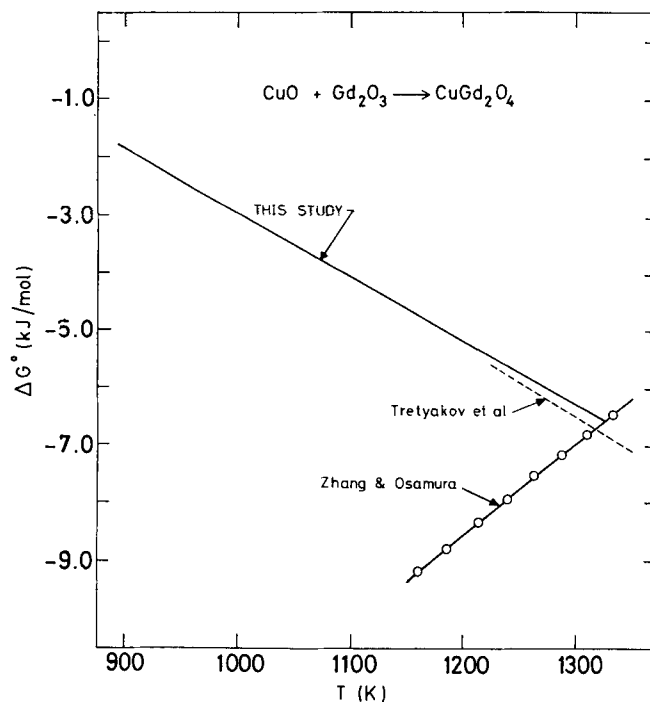


Fig. 3—The variation of the standard Gibbs energy of formation of  $\text{CuGd}_2\text{O}_4$  from component oxides with temperature.

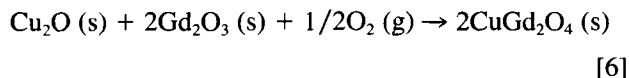
**Table I. Gibbs Energy Change for the Dissociation of CuO :  $4\text{CuO (s)} \rightarrow 2\text{Cu}_2\text{O (s)} + \text{O}_2 \text{(g)}$**

Investigators	Expression for $\Delta G^\circ$ (J/mol)	$\Delta G^\circ$ (J/mol)		
		1300 K	1200 K	1100 K
Jacob and Alcock <sup>[22]</sup>	$260,640 - 187.64T (\pm 420)$	16,708	35,472	54,236
Tretyakov <i>et al.</i> <sup>[18]</sup>	$269,468 - 195.44T (\pm 230)$	15,396	34,940	54,484
Zhang and Osamura <sup>[19]</sup>	$258,370 - 186.0 T (\pm 500)$	16,570	35,170	53,770

effect on atmospheric pressure. Alternatively, pressure inside the apparatus can be maintained at  $1.01 \times 10^5$  Pa by suitable controls. Tretyakov *et al.*<sup>[18]</sup> do not report any of these finer points in their article.

The Gibbs free energy change for Reaction [4] evaluated from the measurements of Zhang and Osamura<sup>[19]</sup> agrees exactly with the present measurements at 1325 K. However, the temperature dependence of the Gibbs energy obtained in the two studies is entirely different. Since the data from Zhang and Osamura<sup>[19]</sup> were derived by combining two separate dissociation temperature measurements, it would be fruitful to compare each of these measurements separately. The free energy change accompanying the dissociation of CuO to  $\text{Cu}_2\text{O}$  obtained by Zhang and Osamura<sup>[19]</sup> is compared with that reported by Jacob and Alcock<sup>[22]</sup> and Tretyakov *et al.*<sup>[18]</sup> in Table I. The agreement between the results of Zhang and Osamura<sup>[19]</sup> and Jacob and Alcock<sup>[22]</sup> are well within the combined error limits and does not explain the discrepancy seen in Figure 3.

The oxygen partial pressure corresponding to the measuring electrode of cell I is defined by the reaction



The value of chemical potential of oxygen, obtained by combining the emf data with the free energy of dissociation of CuO from Jacob and Alcock,<sup>[22]</sup> is given by

$$\begin{aligned} \Delta\mu_{\text{O}_2} &= RT \ln P_{\text{O}_2} \\ &= -227,968 + 143.2T (\pm 500) \text{ J mol}^{-1} \quad [7] \end{aligned}$$

The variation of Gibbs free energy change for Reaction [6] is displayed in Figure 4 in comparison with those reported by Zhang and Osamura<sup>[19]</sup> and Tretyakov *et al.*<sup>[18]</sup> Again, the results of the present study are in good agreement with those of Tretyakov *et al.*<sup>[18]</sup> The measurements of Zhang and Osamura<sup>[19]</sup> agree at high temperature (1325 K) but differ substantially at lower temperatures. Zhang and Osamura<sup>[19]</sup> used a dynamic technique (TG-DTA) for measuring the dissociation temperature in gas atmospheres with defined partial pressures of oxygen. The heating rate was  $0.083 \text{ K s}^{-1}$  ( $5 \text{ K min}^{-1}$ ). Unless the decomposition of  $\text{CuGd}_2\text{O}_4$  is rapid, the dynamic technique will tend to record a higher decomposition temperature and a more negative Gibbs energy change for Reaction [6]. From the results depicted in Figure 4, it appears that the dynamic technique used by Zhang and Osamura<sup>[19]</sup> is satisfactory at high temperature (1325 K). However, at lower temperatures, the measured decomposition temperatures are higher,

probably because of a slower rate of decomposition of  $\text{CuGd}_2\text{O}_4$ .

Zhang and Osamura<sup>[19]</sup> used Ar +  $\text{O}_2$  gas mixtures to vary the partial pressure of oxygen over their samples. For the dissociation measurements on CuO, oxygen partial pressures above  $2 \times 10^3$  Pa were used. For studies on  $\text{CuGd}_2\text{O}_4$ , lower oxygen partial pressures ( $P_{\text{O}_2} > 60$  Pa) were employed. At such low oxygen partial pressures, the ability of Ar +  $\text{O}_2$  mixtures to impose an oxygen potential on a condensed phase is limited. As shown by Akila *et al.*,<sup>[23]</sup> the thermodynamic capacity of oxygen defined by  $C_{\text{O}_2} = (\partial n_{\text{O}_2} / \partial \mu_{\text{O}_2})_{P,T}$  decreases rapidly with the partial pressure of oxygen in Ar +  $\text{O}_2$  mixtures. In the expression for oxygen capacity ( $C_{\text{O}_2}$ ),  $n_{\text{O}_2}$  represents moles of oxygen and  $\mu_{\text{O}_2}$  is its chemical potential. The low oxygen capacity of Ar +  $\text{O}_2$  mixtures implies that, at the gas boundary layer adjacent to solid, the oxygen potential would be substantially higher than that calculated from the gas composition. Therefore, the measured decomposition temperatures would be higher. The error from this source will be maximum at low temperature, where dilute Ar +  $\text{O}_2$  mixtures were employed. In summary, the discrepancy between the results of Zhang and Osamura<sup>[19]</sup> and those obtained in this study at lower temperatures may be attributed to both the slow decomposition kinetics and low thermodynamic capacity of oxygen in dilute Ar +  $\text{O}_2$  gas mixtures.

### C. Oxygen Potential Diagram

Using thermodynamic data obtained in this study for  $\text{CuGd}_2\text{O}_4$  and auxiliary data for CuO,  $\text{Cu}_2\text{O}$ , and  $\text{Gd}_2\text{O}_3$  from the literature,<sup>[22,24,25]</sup> the partial pressures of oxygen for several three-phase equilibria were computed at 1273 K. Since 1 mole of CuO gives 0.5 mole of  $\text{Cu}_2\text{O}$  or 1 mole of Cu on dissociation, the number of moles of Cu remains unchanged when 1 mole of CuO, 0.5 mole of  $\text{Cu}_2\text{O}$ , or 1 mole of Cu is chosen as one of the components. Hence, the composition of ternary mixtures can be expressed in terms of  $\text{CuO} + 1/2\text{Cu}_2\text{O} + \text{Cu}$  and  $\text{GdO}_{1.5}$  in order to facilitate two-dimensional representation. The computed oxygen potential diagram is shown in Figure 5.

When three condensed phases and a gas phase are in equilibrium in a ternary system such as Cu-Gd-O, the system is monovariant: at a given temperature, three condensed phases coexist at a unique partial pressure of oxygen. The three-phase equilibria are therefore represented by horizontal lines in the oxygen potential diagram. At 1273 K, the liquid oxide phase is not stable. It is interesting to note that  $\text{CuGd}_2\text{O}_4$  does not coexist with solid copper.

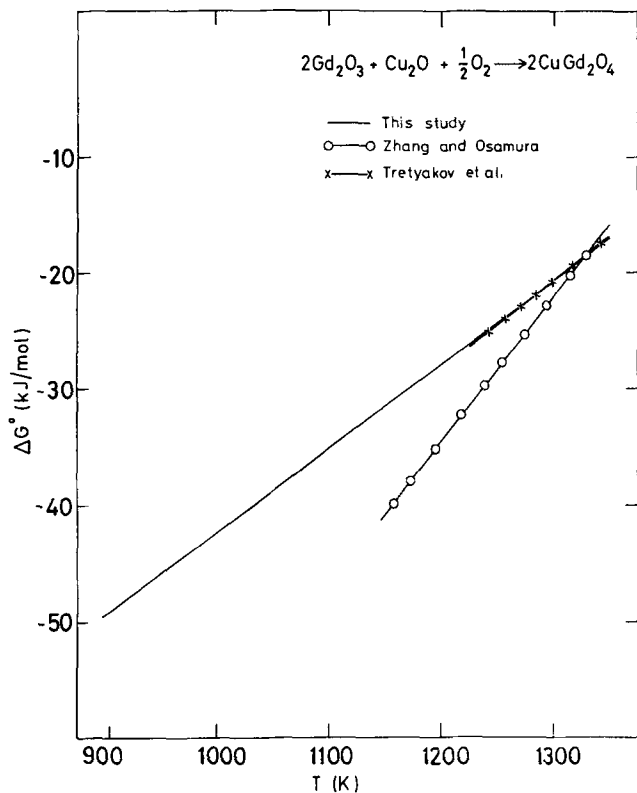


Fig. 4—The temperature dependence of Gibbs free energy change for the reaction  $\text{Cu}_2\text{O} (s) + 2 \text{Gd}_2\text{O}_3 (s) + 1/2\text{O}_2 (g) \rightarrow 2 \text{CuGd}_2\text{O}_4 (s)$ .

#### IV. CONCLUSIONS

The phase diagram for the system Cu-Gd-O at 1273 K has been determined by identifying coexisting phases in equilibrated samples. Only one stable ternary compound,  $\text{CuGd}_2\text{O}_4$ , was identified. The Gibbs free energy of formation of  $\text{CuGd}_2\text{O}_4$  from its component oxides has been determined by an emf technique. The formation of  $\text{CuGd}_2\text{O}_4$  from component oxides  $\text{CuO}$  and  $\text{Gd}_2\text{O}_3$  is endothermic. The compound is entropy stabilized at high temperature. The results of this study are in good agreement with those of Tretyakov *et al.*<sup>[18]</sup> The reasons for the difference between the results of this study and that of Zhang and Osamura are explained. Based on the thermodynamic data obtained in this study and auxiliary information from the literature, an oxygen potential diagram at 1273 K has been constructed for the Cu-Gd-O system.

#### ACKNOWLEDGMENTS

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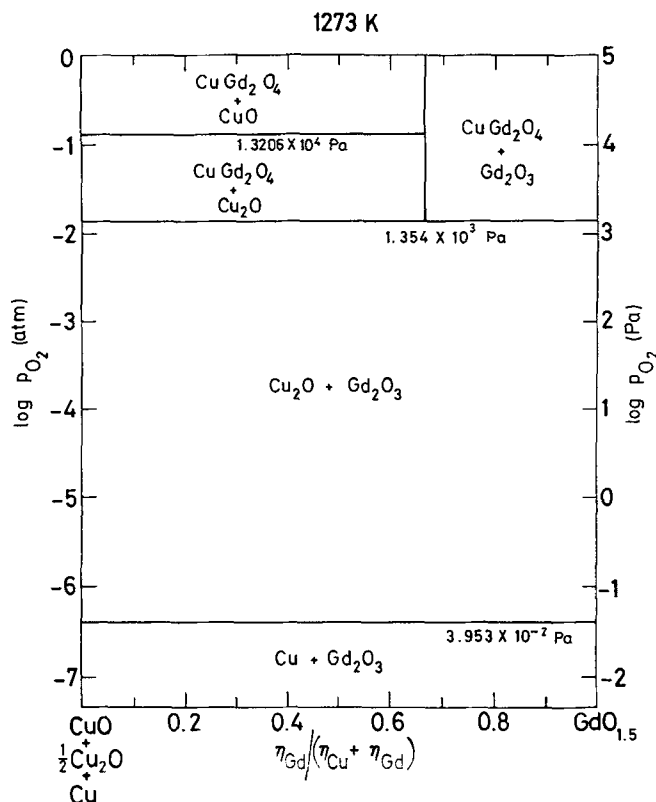


Fig. 5—The oxygen potential diagram for the system Cu-Gd-O at 1273 K.

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