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Phase Equilibria and Thermodynamics of Coexisting Phases in Rare-Earth Element–Iron–Oxygen Systems. III. The Europium–Iron–Oxygen System*

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X-ray and microstructural analysis methods were used to study the possibility of cationic nonstoichiometry in intermediate phases of the ferroperovskite–ferrogarnet type of the Eu_2O_3–Fe_2O_3 system. It is shown that at 1350°C europium ferroperovskite has a narrow range of nonstoichiometry in the direction of excess iron oxide. The character of phase changes in the Eu–Fe–O system during changes in P_{O_2} has been studied; the equilibrium pressure of oxygen on ferrogarnet and magnetite has been calculated, and an equilibrium phase diagram of the type $\log P_{O_2} = f(\text{composition})$ at 1473°K has been constructed. The relative stability of europium ferroperovskite and ferrogarnet has been evaluated.

Introduction

The first attempts to study systems containing a rare-earth element oxide and iron oxide systematically were undertaken by Beretka (*1*). In the Eu–Fe–O system he discovered two intermediate compounds: ferrogarnet $Eu_3Fe_5O_{12}$ and a ferrite with perovskite structure $EuFeO_3$.

Study of the phase equilibria and the construction of an isothermal cross section of part of the phase diagram of the Eu–Fe–O system at 1200°C in the range EuO–Eu_2O_3–Fe_2O_3–Fe were done by McCarthy and Fisher (*2*). The diagram which they constructed permits one, in principle, to establish the equilibrium phase constitution of any composition of condensed phases with a known ratio of Eu:Fe:O. As for intermediate compounds, Ref. (*2*) established the existence of two ternary compounds: orthoferrite $EuFeO_3$ with a perovskite structure and ferrogarnet $Eu_3Fe_5O_{12}$. Nevertheless, information was lacking which would allow one to judge the character of phase changes in the Eu–Fe–O system upon changes in the partial oxygen pressure and the possible solubility of the sesquioxides Eu_2O_3 and Fe_2O_3 in the intermediate phases, europium ferroperovskite and ferrogarnet.

The goal of the present work was to fill the gap mentioned above. In this connection our attention was concentrated on investigation of three basic aspects related to the diagram and to the thermodynamics of coexisting phases in the Eu–Fe–O system:

(1) clarification of the possibility of cationic nonstoichiometry in the intermediate phases of the ferroperovskite and ferrogarnet type of the Eu_2O_3–Fe_2O_3 system;

(2) study of the character of phase changes in the Eu–Fe–O system on change of P_{O_2} and construction of an equilibrium state diagram of the type $\log P_{O_2} = f(\text{composition})$;

(3) evaluation of the relative stability of europium ferroperovskite and ferrogarnet.

Experimental

As starting materials for preparation of the specimens examined, we used Eu_2O_3 with impurity content <0.002% by weight and Fe_2O_3 obtained by thermal decomposition of Mohr's salt (impurity content <0.002% by

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TABLE I

INITIAL MIXING RATIOS OF SPECIMENS INVESTIGATED

Specimens of orthoferrite series		Specimens of garnet series	
No. of the Specimen	Eu/Fe in atomic ratios	No. of the Specimen	Eu/Fe atomic ratios
P-1	1:1	G-1	3:5
P-2	1:1.02	G-2	2.99:5
P-3	1:1.03	G-3	2.98:5
P-4	1:1.05	G-4	2.97:5
P-5	1:1.07	G-5	2.96:5
P-6	1:1.09	G-6	2.95:5
P-7	1:1.12	G-7	2.93:5
P-8	1:0.98	G-8	3.01:5
P-9	1:0.97	G-9	3.02:5
P-10	1:0.95	G-10	3.04:5
P-11	1:0.93		
P-12	1:0.90		

weight) at 800°C for a period of 5 hr in air. The completeness of decomposition of the sulfates was checked by reaction with $BaCl_2$.

To prepare the europium orthoferrite and garnet with excess and with deficit of iron oxide we undertook the following procedure. A large quantity of a mechanical mixture of oxides with proportions of Eu/Fe of 1:1 and 3:5 (corresponding to stoichiometric specimens of orthoferrite and ferrogarnet, respectively) was carefully prepared. Homogenization took place during a 2-hr dry grinding in a ball mill. Then, a strictly determined deficit of Eu_2O_3 or Fe_2O_3 was added to an aliquot of the prepared mechanical oxide mixture, and each composition was homogenized in an agate mortar under ether for a period of 2.5 hr. The specimens were pressed into tablets 8 mm in diameter and 3–3.5 mm high; pressing pressure was 1 t/cm^2. The europium orthoferrite specimens, series P-1–P-12 of Table I, were heated at 1350°C for a period of 10 hr, after which they underwent rapid quenching. The Eu/Fe garnet specimens, series G-1–G-10 of Table I, were carefully heated at 1350°C for a period of 6 hr, after which they were thoroughly ground, homogenized, and again pressed into tablets (pressing pressure, 5 t/cm^2). A second heating of the garnet specimens was done for 8 hr at 1380°C, after which the specimens were rapidly quenched by being thrown into water. All compositions were heated in air ($P_{O_2} = 0.21$ atm) at maximum temperatures but under conditions that precluded dissociation of the sesquioxides and fusion of the phases being formed.

X-ray analysis of the quenched specimens was done with FeK_α radiation. Photographic filming was done in a high resolution camera of diameter 143.25 mm with FeK_α radiation.

Results and Evaluation

Results of X-ray analysis of the perovskite specimens with an excess and with a deficit of Fe_2O_3 are shown in Table II. From this table it can be seen that a garnet phase detectable by X-ray appears at an atomic ratio of Eu/Fe $\geqslant$ 1:1.03. For studying specimens with an Eu/Fe ratio $\leqslant$ 1:1.02, microstructural investigation was used. It showed that in specimens P-8–P-12 one observes inclusions of a second phase with low reflecting capability (europium oxide) in the form of agglomerate and fine grains. A tendency to increase the quantity of this phase in proportion to an increase in the Eu/Fe ratio was observed. Thus,

TABLE II

PHASE COMPOSITION OF PRODUCTS OF THE INTERACTION OF Eu_2O_3 WITH Fe_2O_3 TAKEN IN RATIOS CLOSE TO EQUIATOMIC

No. of the Specimen	Eu/Fe in atomic ratios	X-ray analysis data
P-7	1:1.12	$EuFeO_3 + Eu_3Fe_5O_{12}$
P-6	1:1.09	$EuFeO_3 + Eu_3Fe_5O_{12}$
P-5	1:1.07	$EuFeO_3$ + little $Eu_3Fe_5O_{12}$
P-4	1:1.05	$EuFeO_3$ + traces of $Eu_3Fe_5O_{12}$
P-3	1:1.03	$EuFeO_3$ + traces of $Eu_3Fe_5O_{12}$
P-2	1:1.02	$EuFeO_3$
P-1	1:1	$EuFeO_3$
P-8	1:0.98	$EuFeO_3$
P-9	1:0.97	$EuFeO_3$
P-10	1:0.95	$EuFeO_3$
P-11	1:0.93	$EuFeO_3$
P-12	1:0.90	$EuFeO_3$

the microstructural analysis disclosed the presence of a second phase in specimens beginning with a composition of Eu/Fe = 1:0.98. As density measurements indicate, inclusion of europium oxide at a ratio of 1:0.98 already hinders agglomeration.

Within the limits of sensitivity of the experimental methods used (phase and microstructural analyses), the specimens in the composition range $1:0.99 \leqslant \mathrm{Eu/Fe} \leqslant 1:1.02$ appear to be single-phase perovskite.

To detect a change in lattice parameters in the specimens with varying iron oxide content, specimens P-7 and P-12, P-1 and P-14, as well as P-1 and P-2 were X-rayed together using the photographic method. In specimens with an Eu/Fe ratio equal to 1:1.12 and 1:0.90 a small difference in lattice parameters was observed in the direction of increase ($\leqslant 0.001$ Å) for specimens of Eu/Fe = 1:0.90. In specimens with an Eu/Fe ratio equal to 1:1 and 1:0.5, photographed together, we were able to detect a shift of lines, but in specimens with an Eu/Fe ratio equal to 1:1 and 1:1.02, photographed together, a clear shift of lines was not observed.

Considering the significant difference in ionic radii of Fe^{3+} ($r = 0.73$ Å) and Eu^{3+} ($r = 0.95$ Å), it can be asserted that dissolving excess Fe_2O_3 according to the quasichemical reaction

$$\mathrm{Fe_2O_3\,(in\ EuFeO_3)} \rightarrow \mathrm{Fe}_{\mathrm{Eu}}^{\times} + \mathrm{Fe}_{\mathrm{Fe}}^{\times} + 3\mathrm{O}_{\mathrm{O}}^{\times} \tag{1}$$

or excess Eu_2O_3 according to the quasichemical reaction

$$\mathrm{Eu_2O_3\,(in\ EuFeO_3)} \rightarrow \mathrm{Eu}_{\mathrm{Eu}}^{\times} + \mathrm{Eu}_{\mathrm{Fe}}^{\times} + 3\mathrm{O}_{\mathrm{O}}^{\times} \tag{2}$$

should show up as a change in the lattice parameter of the europium orthoferrite. The fact that in the filming of specimens side by side, one detects a change in the lattice parameters and, second, this change of parameters is extremely small gives evidence of the fact that a zone of homogeneity does exist in europium orthoferrite but it is extremely narrow. Most likely this zone expands in the direction of excess Fe_2O_3 but this excess does not exceed 1%, i.e., single-phase ferroperovskite at 1350°C exists in a range of composition from $Eu_2O_3 \cdot Fe_2O_3$ to $Eu_2O_3 \cdot 1.01Fe_2O_3$.

Table III presents the phase composition of the products of interaction of Eu_2O_3 with Fe_2O_3 for Eu/Fe ratios close to 3:5. It is easy to see that at Eu/Fe ratios $\geqslant 3.02:5$, a perovskite phase appears along with a garnet. With excess Fe_2O_3, a second phase (α-Fe_2O_3) becomes distinguishable by X-ray at a composition of Eu/Fe $\leqslant 2.95:5$. To study the range of compositions which, according to X-ray analysis, are single phase (2.96:5–3.01:5), microstructural investigations of a series of specimens were undertaken. It turned out that specimen G-1 (Eu/Fe = 3:5) seems to be practically single-phase garnet; specimen G-9 (Eu/Fe = 3.02:5) contains, along with the basic garnet phase, inclusions of: (a) a phase with high reflective ability present in very small amounts (α-Fe_2O_3) and (b) angular formations which represent coalescence of two phases, garnet with Fe_3O_4 or $EuFeO_3$. Specimens G-3 and G-6 (Eu/Fe = 2.98:5 and 2.95:5) have practically the same structure. In them, along with garnet, are observed separate small grains of α-Fe_2O_3.

TABLE III

PHASE COMPOSITION OF PRODUCTS OF THE INTERACTION OF Eu_2O_3 AND Fe_2O_3 TAKEN AT A RATIO CLOSE TO THE STOICHIOMETRY OF GARNET

No. of the Specimen	Eu/Fe in atomic ratios	X-ray analysis data
G-10	3.04:5	$Eu_3Fe_5O_{12}$ + traces of $EuFeO_3$
G-9	3.02:5	$Eu_3Fe_5O_{12}$ + traces of $EuFeO_3$
G-8	3.01:5	$Eu_3Fe_5O_{12}$
G-1	3:5	$Eu_3Fe_5O_{12}$
G-2	2.99:5	$Eu_3Fe_5O_{12}$
G-3	2.98:5	$Eu_3Fe_5O_{12}$
G-4	2.97:5	$Eu_3Fe_5O_{12}$
G-5	2.96:5	$Eu_3Fe_5O_{12}$
G-6	2.95:5	$Eu_3Fe_5O_{12}$ + traces of α-Fe_2O_3
G-7	2.93:5	$Eu_3Fe_5O_{12}$ + traces of α-Fe_2O_3

Thus, it has been established that specimens beginning with an atomic ratio of Eu/Fe $\leqslant$ 2.98:5 are two phase.

Taking into account that there is great difference in the ionic radii of Eu^{3+} and Fe^{3+}, incorporation of excess Fe_2O_3 into the structure of europium garnet according to the quasichemical equation

$$4Fe_2O_3\,(\text{in } Eu_3Fe_5O_{12}) \rightarrow 5Fe_{Fe}^{\times} + 3Fe_{Eu}^{\times} + 12O_O^{\times} \quad (3)$$

or dissolving of excess Eu_2O_3 according to the quasichemical equation

$$4Eu_2O_3\,(\text{in } Eu_3Fe_5O_{12}) \rightarrow 5Eu_{Fe}^{\times} + 3Eu_{Eu}^{\times} + 12O_O^{\times} \quad (4)$$

should lead to noticeable change in the cubic lattice parameters of the garnet.

To detect the parameter changes of the lattice, specimens G-7 and G-10 as well as G-7 and G-1 were filmed together. There was no success in observing any distinct change in lattice parameter whatsoever. In all the specimens filmed, the lattice parameter of the garnet phase was equal to $a = 12.4980 \pm 0.0005$ Å, which agrees very well with the data of Ref. (*2*) and (*3*).

The fact that a change in lattice parameter could not be observed (although it should have been expected from dissolution of excess Eu_2O_3 and Fe_2O_3 in the ferrogarnet) is evidence of absence of noticeable nonstoichiometry in europium garnet even at maximum temperatures (1380°C) under conditions precluding dissociation of sesquioxides and fusion of ferrogarnet.

It is not without interest to make a comparison of our data with those known in the literature. Data about cationic nonstoichiometry in rare-earth element perovskites is lacking in general; and there are substantial differences on the question of solubility of Fe_2O_3 in the garnet structure. Thus, Paladino (*4*) in his example of iron–yttrium garnet showed that a small zone of homogeneity exists in the direction of excess Fe_2O_3. He detected a zone of homogeneity of yttrium ferrogarnet from Y/Fe 3:5 to 2.97:5 at temperatures of 1450–1475°C. At the same time, Ref. (*5*) maintains that yttrium ferrogarnet has a broad zone of cation homogeneity with excess Y_2O_3 all the way to the composition $Y_{3.4}Fe_{4.6}O_{12}$. The conclusions of Ref (*5*) seem to us not to be very convincing since they are based on data of only microstructural and electromagnetic characteristics, whereas measurements of the lattice parameters, judging by the information in (*5*), were not carried out.

Based on McCarthy's data (*2*) on phase equilibria in the Eu–Fe–O system at 1473°K and on the measurements by (*6*, *12*) of the equilibrium pressure of oxygen over europium orthoferrite and products coexisting with it from dissociation of Eu_2O_3 + Fe (at 1473°K, $\log P_{O_2} = -12.4$), we attempted to construct equilibrium isothermal diagrams $\ln P_{O_2} = f(\xi_{Fe})$ and $\xi_O = f(\xi_{Fe})$. Data absent in the literature on the equilibrium pressure of oxygen over europium ferrogarnet and products coexisting with it from dissociation of $EuFeO_3 + Fe_3O_4$ were filled in from the result of the following approximate calculation.

For the reaction

$$6Eu_3Fe_5O_{12} = 18EuFeO_3 + 4Fe_3O_4 + O_2 \quad (5)$$

the free-energy change is $\Delta G^\circ_{(5)} = -RT \ln P_{O_2}$, from which

$$\log P_{O_2} = -\frac{\Delta G^\circ_{(5)}}{4.575T}. \quad (6)$$

(It is assumed that coexisting condensed phases have stoichiometric composition, expressed by the formulas in Eq. (5) and, consequently, their activity is equal to 1.)

In order to evaluate $\Delta G^\circ_{(5)}$, let us consider the totality of the reactions:

$$\tfrac{1}{2}Eu_2O_3 + \tfrac{1}{2}Fe_2O_3 = EuFeO_3, \quad (7)$$

$$6Fe_2O_3 = 4Fe_3O_4 + O_2, \quad (8)$$

$$\tfrac{3}{2}Eu_2O_3 + \tfrac{5}{2}Fe_2O_3 = Eu_3Fe_5O_{12}. \quad (9)$$

It is evident that

$$\Delta G^\circ_{(5)} = 18\Delta G^\circ_{(7)} + \Delta G^\circ_{(8)} - 6\Delta G^\circ_{(9)}. \quad (10)$$

From the data of (*6*, *12*), it follows that at 1473°K $\Delta G^\circ_{(7)} = -10.4 \pm 0.14$ kcal/mole. The tabulated value of $\Delta G^\circ_{(8)}$ is 18.2 ± 0.3 kcal/

mole (*7*). We have calculated the magnitude of $\Delta G^\circ_{(9)}$ in the following manner. From Kesler's thermodynamic measurements (*8*), it follows that at 975°K, $\Delta H^\circ_{(7)} = -3.6$ kcal/mole. Assuming that (a) $\Delta H^\circ_{(7)}$ depends very little on temperature within the range 975–1473°K and that (b) $\Delta H^\circ_{(9)} \simeq 4\Delta H^\circ_{(7)}$, we find at 1473°K that $\Delta H^\circ_{(9)} = -14.4$ kcal/mole. Using data (*15*) on measurement of heat capacity of $Eu_3Fe_5O_{12}$ and extrapolating them to a temperature of 1473°K, we find $\Delta S^\circ_{(9)} = 11.6$ entropy units. Taking into account that $\Delta G^\circ_{(9)} = \Delta H^\circ_{(9)} - T\Delta S^\circ_{(9)}$ and using the values presented above for $\Delta H^\circ_{(9)}$ and $\Delta S^\circ_{(9)}$, we get $\Delta G^\circ_{(9)} = -31.8$ kcal/mole. From Eq. (10) it follows that $\Delta G^\circ_{(5)} = -(18)(10.4) + 18.2 + (6)(31.8) = 21.8$ kcal/mole.

Then in agreement with Eq. (6), the equilibrium pressure of oxygen over ferrogarnet and magnetite is

$$\log P_{O_2} = \frac{-21\,800}{(4.575)(1473)} = -3.3. \qquad (11)$$

It may be shown further that for the reaction

$$\begin{aligned} &3EuFeO_3 + Fe_2O_3 = Eu_3Fe_5O_{12}, \\ &\Delta G^\circ_{(12)} = \Delta G^\circ_{(9)} - 3\Delta G^\circ_{(7)} \qquad (12) \\ &\quad = -0.6\ \text{kcal/mole (at 1473°K)}. \end{aligned}$$

It was of interest to compare $a_{Fe_2O_3}$ in the ferrogarnet $Eu_3Fe_5O_{12}$ and in the ferroperovskite $EuFeO_3$.

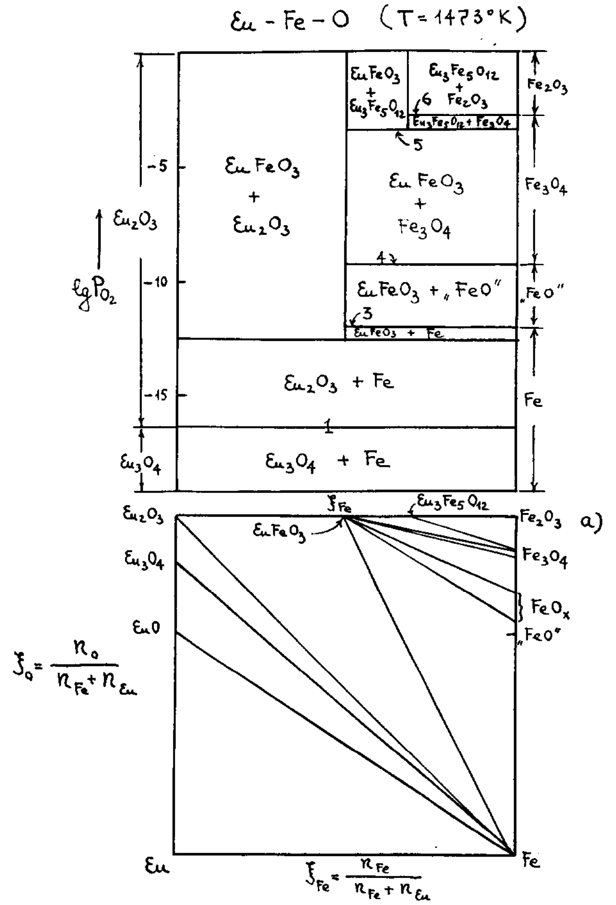

FIG. 1. Equilibrium diagrams of log $P_{O_2} = f(\xi_{Fe})$ and (a) $\xi_O = f(\xi_{Fe})$ of the Eu–Fe–O system at 1473°K.

For the ferrogarnet, in equilibrium with orthoferrite,

$$\Delta G^\circ_{(12)} = -RT\ln K_{p(12)}$$

$$= -4.575\,T\log\frac{a_{Eu_3Fe_5O_{12}}}{(a_{EuFeO_3})(a_{Fe_2O_3})}$$

$$= \frac{(4.575)(1473)}{2}\log a_{Fe_2O_3}$$

from which

$$\log a_{Fe_2O_3} = \frac{-600}{(4.575)(1473)}$$

$$= -0.089;\quad a_{Fe_2O_3} = 0.81.$$

For the ferroperovskite in equilibrium with Eu_2O_3

$$\Delta G^\circ_{(7)} = -RT\ln K_{p(7)}$$

$$= -4.575\,T\log\frac{a_{EuFeO_3}}{a^{1/2}_{Eu_2O_3}a^{1/2}_{Fe_2O_3}}$$

$$= \frac{(4.575)(1473)}{2}\log a_{Fe_2O_3}$$

from which

$$\log a_{Fe_2O_3} = \frac{(2)(10\,400)}{(4.575)(1473)} = -3.0;$$

$$a_{Fe_2O_3} = 1\times 10^{-3}.$$

Thus, the binding of hematite to ferrogarnet lowers the activity of Fe_2O_3 compared to pure hematite at least 1.2 times, whereas during orthoferrite formation, the activity of Fe_2O_3 diminishes 1000 times. These data also characterize the relative difference in stability of ferrogarnet and ferroperovskite.

In Fig. 1 are presented equilibrium diagrams of $\log P_{O_2} = f(\xi_{Fe})$ and $\xi_O = f(\xi_{Fe})$, where $\xi_{Fe} = n_{Fe}/(n_{Fe}+n_{Eu})$, for the Eu–Fe–O system at 1473°K. These diagrams differ noticeably from analogous diagrams for the Ce–Fe–O (*13*) and Pr–Fe–O (*14*) systems. Thus, at very low partial oxygen pressures, iron coexists with the oxide Eu_3O_4 in the Eu–Fe–O system, but nothing similar exists in the Ce–Fe–O and Pr–Fe–O systems. Europium sesquioxide forms only at $-\log P_{O_2} \leqslant 16.5$. The europium orthoferrite which appears instead at $-\log P_{O_2} \leqslant 12.4$ is not inclined at all to oxidation. For initial compositions with $\xi_{Fe} \geqslant 0.5$ at $-\log P_{O_2} \leqslant 3.3$ complications arise in the Eu–Fe–O system in connection with appearance of ferrogarnet. Table IV shows a summary of the fixed points of the diagram of the Eu–Fe–O system presented in Fig. 1.

TABLE IV

A SUMMARY OF THE FIXED POINTS OF THE DIAGRAM OF THE Eu–Fe–O SYSTEM (FIG. 1)

Point	Equation $\log P_{O_2} = A - B/T$		$-\log P_{O_2}$ at 1473°K	Source
	A	B		
1			16.50	(*11*)
2	9.04	31 547	12.40	(*6, 12*)
3	6.78	27 600	11.90	(*7, 10*)
4	11.06	31 090	9.20	(*7, 10*)
5			3.30	Our calculations
6	14.90	25 900	2.70	(*7, 10*)

Despite the known tendency of europium to a divalent state, which is the reason for formation of a phase of the type $LnFe_{12}O_{19}$ with magnetoplumbite structure (*9*), we have established that the compound $EuFe_{12}O_{19}$ does not exist. Rather, a mixture of oxides of total composition "$EuFe_{12}O_{19}$," after thermal treatment at various temperatures for a period of time long enough to assure reaching equilibrium, consists of three coexisting phases, ferrogarnet, magnetite, and hematite. The authors of Ref. (*2*) also came to an analogous conclusion about the relative possibility of forming a phase of the $EuFe_{12}O_{19}$ type in the Eu–Fe–O system.

Conclusions

The nonstoichiometry of intermediate phases in the Eu_2O_3–Fe_2O_3 system has been studied and it has been shown that single-phase ferroperovskite at 1350°C has a narrow zone of nonstoichiometry in the direction of excess iron oxide.

The equilibrium pressure of oxygen over ferrogarnet and magnetite has been calculated, the equilibrium diagrams $\log P_{O_2} = f(\xi_{Fe})$ and $\xi_O = f(\xi_{Fe})$ for the Eu–Fe–O system at 1473°K have been constructed, and the relative stability of europium ferroperovskite and ferrogarnet has been evaluated.

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