

Synthesis of Rare Earth Monoxides

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The standard Gibbs energy changes for the formation of an ionic or metallic monoxide from rare earth metal and sesquioxide have been calculated. Under high pressures ionic ytterbium monoxide and lighter rare earth metallic monoxides should be obtained, which is confirmed by experiments in a belt-type apparatus in the range 15–80 kbar and 500–1200°C. For $L_n = \text{La, Ce, Pr, Nd, Sm}$, a face-centered cubic compound is obtained from each reaction. The cell parameters are respectively 5.144, 5.089, 5.031, 4.994, and 4.943 ± 0.005 Å. The compounds appear golden yellow with a metallic luster. From chemical analyses and cell parameter consideration it is concluded that these compounds are the rare earth monoxides. For $L_n = \text{Gd, Dy, Tm}$, no reaction is observed at 50 kbar and 1000°C. The rare earth monoxides show a variety of properties: LaO, CeO, PrO, and NdO are metallic with the rare earth in the trivalent state; EuO and YbO are semiconductors with the rare earth in the divalent state; SmO is metallic with samarium in an intermediate valence state close to 3.

I. Thermodynamic Stability of Divalent Rare Earth Monoxides

The synthesis under normal pressure of bulk rare earth monoxides has been attempted many times but, except for EuO, the existence of which is firmly established, it was shown that the compounds obtained were oxidenitrides (1) and so the occurrence of these monoxides is controverted (2, 3). The synthesis of YbO was reported (4) and then questioned (5, 6). However, it seems that this monoxide can be obtained (7, 8), but always mixed with some sesquioxide. The occurrence of face-centered cubic (fcc) compounds in rare earth thin films studied by electron microscopy was ascribed to rare earth monoxides (9–11) but these fcc patterns are rather to be attributed to nonstoichiometric cubic hydrides (12) or to the oxidation of hydrides (13) into *C*-type sesquioxides. Thus, grounds for re-

jecting the existence of lower rare earth oxides at atmospheric pressure have so far been established and only the existence of EuO is beyond dispute. This conclusion is supported by thermodynamic considerations which show that divalent rare earth monoxides, except for EuO and perhaps YbO, should be unstable.

The thermodynamic stabilities of rare earth monoxides have been calculated with respect to disproportionation into metal and sesquioxide, or inversely whether the preparation of monoxide by reduction of sesquioxide with pure metal was possible. A negative value of the standard Gibbs energy for a reaction indicates that the product phase is stable at normal pressure; on the other hand a positive value shows that the new phase is not stable at normal pressure but does not preclude its preparation under other conditions, such as under high pressure, with subsequent mainte-

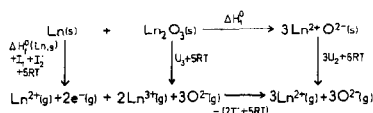
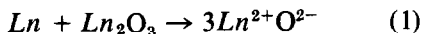


FIG. 1. Thermodynamic cycle for the formation of an ionic rare earth monoxide from metal and sesquioxide.

nance in a metastable state under normal conditions.

The standard Gibbs energy change ΔG°_1 for the reaction



has been determined using different methods under the assumption that the rare earth ion is in the divalent state in the monoxide. In the cases of samarium, europium, and ytterbium monoxides all the thermodynamic data needed for the calculation are available except for the lattice energies, which can be determined using a Kaputinskii treatment. For EuO the values so obtained are negative, -42 (3) or -157 kJ (14); they are positive for SmO ($+29$ kJ (3)) and YbO ($+54$ (3) or $+33$ kJ (15)) but are small and somewhat inconclusive as they are of the same order of, or even less than, the probable errors in the calculation.

The standard enthalpy change ΔH°_1 for the formation reaction (1) can be analyzed by the thermodynamic cycle of Fig. 1. The equation

$$\Delta H^\circ_1 = \Delta H^\circ_f(\text{Ln}, \text{g}) + I_1 + I_2' + I_3' + U_3 - 3U_2 - RT - 3I_3'$$

is obtained, where $\Delta H^\circ_f(\text{Ln}, \text{g})$ is the enthalpy of atomization of the metal; U_2 and U_3 are the lattice energies of the monoxide and the sesquioxide; I_1 , I_2' , I_3' are respectively the first, second, and third ionization potentials of the rare earth element, where the prime indicates that the electron is lost from a dipositive ion of configuration $[\text{Xe}]4f^{n+1}$, with n the number of $4f$ electrons carried by the tripositive ion in its ground

state. The standard Gibbs energy change for reaction (1) is given by

$$\Delta G^\circ_1 = \Delta H^\circ_1 - T\Delta S^\circ_1,$$

where ΔS°_1 is the entropy change for reaction (1). For europium the term $T\Delta S^\circ_1$ can be evaluated from available data (16, 17). It is small (approximately 7 kJ) and in the lanthanide series it should be nearly constant if the small irregularities caused by magnetic or crystallographic phase transitions are ignored. Thus the standard Gibbs energy change for reaction (1) can be written as

$$\Delta G^\circ_1 = \Delta H^\circ_f(\text{Ln}, \text{g}) + I_1 + I_2' + I_3' + U_3 - 3U_2 - C - 3I_3',$$

where C is a constant ($+10$ kJ).

The values of the enthalpies of atomization (18) and the ionization potentials of the lanthanides (19) ($I_1 + I_2' + I_3' = I_1 + I_2 + I_3$) have been determined accurately. I_3' is equal to I_3 except for lanthanum and gadolinium where it is reduced by 85.7 and 28.5 kJ according to Johnson (16). The values of the lattice energies of the sesquioxides U_3 have been calculated from Born-Haber cycles for the formation of cubic sesquioxides or from a Madelung-type relation corrected for systematic errors (18). U_2 (EuO) can be calculated from a Born-Haber cycle,

$$\begin{aligned}
 U_2(\text{EuO}) &= \Delta H^\circ_f(\text{EuO}) \\
 &- \Delta H^\circ_f(\text{Eu}, \text{g}) - (I_1 + I_2) \\
 &- \Delta H^\circ_f(\text{O}, \text{g}) - EA + 2RT,
 \end{aligned}$$

with

$$\Delta H^\circ_f(\text{EuO}) = -591.8 \text{ kJ} \quad (16),$$

$$\Delta H^\circ_f(\text{O}, \text{g})$$

$$+ EA - 2RT = 1068.2 \text{ kJ} \quad (18)$$

so

$$U_2(\text{EuO}) = -3468.2 \text{ kJ}.$$

For the remaining monoxides U_2 can be calculated from the Kaputinskii relation

$$U_2 = \frac{A}{r_+ + r_-} \left[1 - \frac{0.345}{r_+ + r_-} \right],$$

where r_- is the radius of the oxygen ion (1.40 Å) and r_+ is the radius of the rare earth divalent ion. This radius is equal to 1.17 Å for europium and 1.038 Å for ytterbium as deduced from the lattice parameter 4.877 Å of YbO (20); it is interpolated and extrapolated to generate r_+ for the other monoxides.

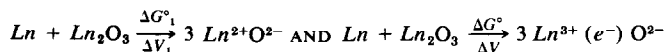
ΔG°_1 can then be calculated: it is positive for all the rare earths except for europium and ytterbium. For the latter element the smallest absolute value is obtained. In this case, and only in this case, the sign of ΔG°_1 depends critically on the choice of the parameters: for example, a different choice of U_3 (U_{calcd} instead of U_{BH} in Ref. (18)) generates a positive value. It seems from experiments that ΔG°_1 should be very close to zero; thus we set ΔG°_1 (Yb) = 0 by correcting U_2 (YbO) (3603 instead of 3625 kJ) and keep the previous values for U_3 . The value of U_2 (EuO) previously determined is thought to be correct as it is deduced from a Born-Haber cycle using accurate ionization potentials. Then the same procedure which was applied to obtain U_3 values (18) is applied: the differences between U_2 for YbO and EuO have been interpolated and extrapolated to generate the U_2 values indicated in Table I.

The values of $K \equiv \Delta H^\circ_f (Ln, g) + I_1 + I'_2 + I'_3 + U_3 - 3U_2$ increase nearly smoothly in the rare earth series except for europium and ytterbium where positive deviations of ~100 and 45 kJ are observed. This behavior is in agreement with Johnson's arguments (16). All the irregularities in ΔG°_1 come from the third ionization potential I'_3 .

The standard Gibbs energy changes for

reaction (1) calculated with this method are indicated (solid line) in Fig. 2. It is found as expected that EuO should be stable and the value of ΔG°_1 so obtained is in good agreement with a previous result (−141 kJ as compared to -155 ± 33 kJ (14)). This analysis reveals clearly that ΔG°_1 is positive for all the other rare earths (except Yb) but including samarium and thulium (+142 and +328 kJ), which form divalent halides. Thus the formation of divalent rare earth monoxides, except for EuO and possibly YbO, is not to be expected under normal conditions. This condition is in agreement with the results of another analysis (21), which, however, appears less accurate. The energy differences between the valence states of rare earth metals have been determined by Johansson (21) by interpolation. This author considers that the quasi-irregular changes in certain thermodynamic properties between neighboring rare earth compounds are due to different valence states of the atoms in the metals. He shows that if the properties are referred to the excited trivalent atomic state (i.e., by adding to the experimental value the excitation energy required for the atomic process $f^{n+1}s^2 \rightarrow f^n ds^2$) one obtains a quite regular variation through the series. Application of this method allows determination of the standard Gibbs energy changes for a large variety of reactions involving hypothetical compounds. In particular, the stability of the monoxides with respect to disproportionation into sesquioxide and metal can be investigated. The variations of the Gibbs energy for reaction (1) are given in Fig. 2 (dashed line). It is found, as expected, that EuO should be stable, but surprisingly that YbO should also be stable, with the ΔG°_1 value (−138 kJ) only slightly less negative than that for EuO. This value is relatively small and the possible errors which have been estimated as approximately 65 kJ must be considered. The agreement with

TABLE I
STANDARD GIBBS ENERGY CHANGES AND VOLUME VARIATIONS FOR THE REACTIONS



	$\Delta H^\circ_f + I_1 + I_2 + I_3$ (kJ)	U_3 (kJ)	U_2 (kJ)	$\Delta H^\circ_f + I_1 + I_2 + I_3 + U_3 - 3U_2 = K$ (kJ)	I'_3 (kJ)	ΔG°_1 (kJ)	ΔG° (kJ)	M (kJ)	ΔV_1 (cm ³)	ΔV (cm ³)
La	3887	12780	3362	6581	1765	1276	3	5563	-1.6	-10.5
Ce	3943	12897	3379	6703	1949	846	10	5618	~0	-9.2
Pr	3985	13002	3396	6799	2087	528	17	5675	~0	-9.7
Nd	4024	13057	3414	6839	2132	434	24	5694	-0.9	-10
Pm	4057	13148	3432	6909	2152	443	32	5732	-1.4	-10.5
Sm	4076	13200	3450	6926	2258	142	38	5754	-2.6	-10.4
Eu	4213	13275	3468	7084	2405	-141	130	5794	-11.8	—
Gd	4147	13320	3487	7006	1962	1110	53	5813	-3.6	-10.7
Tb	4179	13409	3506	7070	2114	718	60	5849	-3.2	-11.5
Dy	4188	13475	3525	7088	2200	478	67	5873	-4.7	-11.6
Ho	4224	13534	3542	7132	2204	510	74	5903	-4.1	-11.4
Er	4250	13596	3563	7157	2194	565	82	5929	-4.4	-11.4
Tm	4276	13660	3581	7193	2285	328	89	5957	-4.3	-11.2
Yb	4350	13715	3603	7256	2415	~0	138	5983	-11.7	—
Lu	4338	13757	3623	7226	2022	1150	103	6005	-3.7	-11.6

the previous analysis is good especially in the middle of the series.

Are there rare earths for which reaction (1) is possible under high pressure?

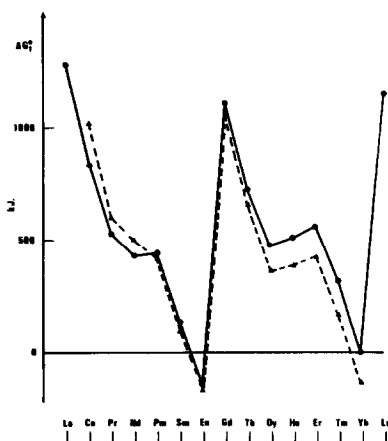


FIG. 2. Standard Gibbs energy change ΔG°_1 for the reaction $Ln + Ln_2O_3 \rightarrow 3 Ln^{2+}O^{2-}$ from two different methods (—, ionization potentials; ---, interpolation).

The effect of pressure is to modify ΔG°_1 by $d(\Delta G^\circ_1) = \Delta V_1 \cdot dP$, where ΔV_1 is the volume difference between the monoxide and the reactants. The monoxide is assumed to have the fcc structure with a cell parameter given by the sum of the ionic radius of the divalent rare earth and that of oxygen. The sesquioxides are supposed to be in the hexagonal or monoclinic phases which are the stable phases under high pressure. In calculating ΔG°_1 we made the assumption that the sesquioxide was in the cubic form but the difference with the actual case would be to add approximately 4 kJ, the difference between $\Delta H^\circ_f(Ln_2O_3, \text{hex})$ and $\Delta H^\circ_f(Ln_2O_3, \text{C})$. This does not modify the results. The term ΔV_1 (Table I) is negative; it is weak for all the rare earths except for europium and ytterbium. The effect of pressure is then to reduce ΔG°_1 but appreciably only for these two metals. For europium ΔG°_1 was already negative. For ytterbium ΔG_1 is decreased to -57 kJ at a

pressure of 50 kbar and consequently YbO should be stable at these conditions. In fact ΔV_1 decreases with pressure as the bulk modulus of ytterbium metal is smaller than those of the oxides and the decrease in the value of the Gibbs energy change might be less. However, the reduction of ytterbium sesquioxide by metal at pressures as low as 15 kbar has been demonstrated experimentally (20). This observation shows clearly that at normal pressure YbO is very close to stability ($\Delta G^\circ_1 \sim 0$). The volume reductions and the corresponding $P \cdot \Delta V_1$ terms are too small to make ΔG_1 negative for the remaining rare earths, including samarium and thulium.

In conclusion, except for EuO and YbO, no *divalent* rare earth monoxide should be obtained under high pressures.

This analysis is only valid when purely ionic monoxides, $Ln^{2+}O^{2-}$, are considered. It is not necessarily true if the rare earth ions are in the *trivalent* state, as in most of the chalcogenides. Furthermore it has been shown (22) that as the cell parameters of the divalent samarium monochalcogenides decrease with decreasing anionic radius, the *d* band widens. For samarium monoxide it would overlap the *f* level, thus making the compound metallic. Such a state would not be stable and one of higher valence and smaller volume would be expected instead. But because of the volume reduction involved in this reaction, pressure would favor the formation of this trivalent samarium monoxide. The reactions $Ln + Ln_2O_3$ have been performed under high pressure in order to determine if metallic monoxides could be obtained.

II. High-Pressure Experiments

Samples were made of the mixed powders of the reactants. the pure metal was obtained by filing an ingot (Research Chemicals, nominal purity 99.9%) under

controlled argon atmosphere; the sesquioxide (nominal purity 99.95%) was calcined around 1000°C to reduce non-metallic impurities. Generally an excess of metal was added with respect to stoichiometry.

The high-pressure experiments were performed in a compressible gasket apparatus of "belt" type between 10 and 80 kbar. The reaction temperatures varied between 500 and 1200°C. The, approximately 150-mg, sample was placed at the center of the high-pressure cell in a boron nitride crucible inside a tantalum heater tube. This furnace was surrounded by another boron nitride sleeve in order to prevent corrosion of the metallic heater by the decompositional water from the pyrophyllite used as the pressure-transmitting medium. Temperature was measured with a Pt-Pt 10% Rh thermocouple which, to prevent contamination, did not cross the sample. The difference between the temperature so measured and the sample temperature had been calibrated in previous runs. The effect of pressure on the emf of the thermocouple was not taken into account. The pressure was determined from a calibration curve obtained at room temperature by monitoring the discontinuities of the electrical resistivities of bismuth and barium during their polymorphic transitions (25.4, 55, 77 kbar) as a function of the load. The temperature effect on the value of pressure was not considered. Experiments were performed at constant load. Pressure was first set to the desired value and the temperature was then increased slowly. After reaction the temperature was generally gradually decreased, but sometimes quenching was effected by turning off the electrical power. After the sample was unloaded it was crushed in open air and examined with an X-ray diffractometer. The products and starting materials were analyzed chemically for nonmetallic impurities.

The experiments were generally performed at 40–50 kbar and at temperatures as high as possible, but chosen so as to remain below the melting point of the pure metal. The following conditions were thus applied: experiments with lanthanum were made at 40 kbar and 900°C, with praeosodymium at 50 kbar and 800°C, with neodymium at 50 kbar and 1000°C. Reaction time was generally 4 hr. The experiments with lanthanum, cerium, praeosodymium, neodymium, and samarium yielded golden yellow compounds with metallic lusters. The structures are face-centered cubic with lattice parameters of 5.144, 5.089, 5.031, 4.994, and 4.943 Å (± 0.005 Å). No foreign line could be seen in the diffraction patterns except for those of lanthanum and cerium (23) reactions. They were respectively attributed to hexagonal La (OH)₃ and to Ce₂O₃ (hex). The fcc compounds transformed in air into the hexagonal hydroxides but progressively more slowly as one moved from lanthanum to samarium. Reactions with samarium (24) were performed at 1000°C at different pressures; below 50 kbar reaction was incomplete after a 4-hr treatment but was complete above. The reactions with gadolinium, dysprosium, and thulium were studied at 50 kbar and 1000°C but no new product could be detected. Larger ranges of pressure and temperature (10–80 kbar, 600–1200°C) were investigated for thulium but no reaction could be noticed.

Because rare earth metals are well known to form fcc binary and ternary compounds with hydrogen, carbon, or nitrogen, the impurity contents of the products for these three elements were checked by acidimetric or catharometric methods. With neodymium the impurity contents of the starting materials and of the compound obtained under high pressure were almost identical, indicating that contamination due to the pressure treatment was minimal. In the neodymium and samarium cases, the

analytical results of the reaction products were nearly identical and they are thought to be representative of all the rare earth systems investigated as all handling was carried out under identical conditions. A typical analysis of the fcc phase was $H < 3$ at.%, $C \sim 1$ at.%, $N \sim 0.2$ at.%. From these analyses it may be inferred that the fcc compounds obtained are really new rare earth oxides. This conclusion is supported by our experiments with gadolinium, dysprosium, and thulium in which no fcc compounds are found, although the same hydrides, oxide nitrides, etc., also exist for these rare earths and similar conditions of environment, pressure, and temperature were applied in all cases.

The cell parameters of the compounds obtained for $Ln = \text{La to Sm}$ are much smaller than the values calculated for ionic monoxides with the rare earth in the 2+ state, but are larger than these calculated with the trivalent ionic radius of the rare earth. In fact it is not possible to use a sum of ionic radii since the compounds are metallic as demonstrated by the low resistivities of the samples (of the order of 300 $\mu\Omega \cdot \text{cm}$). For calculating the lattice parameters of monoxides we extrapolate (23–25) the cell constants of the chalcogenides, which are metallic when the rare earths are in the trivalent state, as a function of the anionic radius. From lanthanum to neodymium these extrapolations give values which are in excellent agreement with our experimental results. This shows that the new compounds obtained are really the rare earth monoxides and that from lanthanum to neodymium the rare earth is trivalent, which explains the metallic properties.

The cell parameters of rare earth monochalcogenides and monoxides are given in Fig. 3. Three exceptions to the overall well-known lanthanide contraction are observed for SmO, EuO, and YbO. Europium is of course divalent in EuO. This is also the case of ytterbium in YbO, as has already

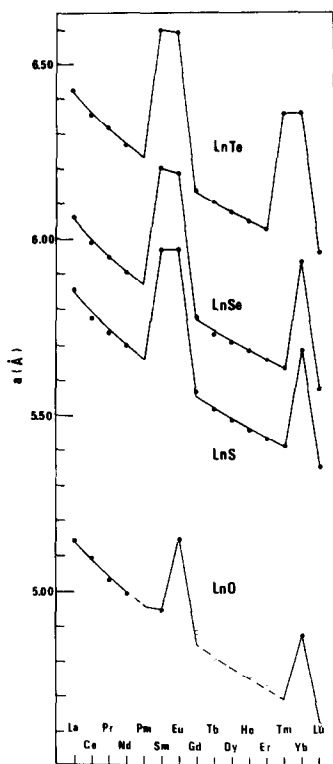


FIG. 3. Cell parameters of rare earth monochalcogenides and monoxides (●, experimental values; ○, values extrapolated from monochalcogenides).

been demonstrated (20). For SmO the cell parameter is slightly larger than the value calculated for a pure trivalent samarium ion. A state of intermediate valence (2.9) has been proposed (24) to account for the difference as all the samarium sites are equivalent and the XPS spectrum shows the presence of 2+ and 3+ samarium ions (25). Such a situation is well known to occur in SmS above 7 kbar where this compound exhibits the same metallic golden aspect as the SmO samples.

No new ionic monoxide in addition to YbO could be made under pressure, as predicted from the Gibbs energy calculations. We now examine why the synthesis of metallic monoxides is possible under high pressures and if new ones could be expected.

III. Thermodynamic Stability of Trivalent Rare Earth Monoxides

At ordinary pressure, except for europium, the pure rare earth metal does not react with the sesquioxide and it is impossible to obtain monoxides, either metallic or ionic. This shows, as for reaction 1, the standard Gibbs energy change ΔG° for the reaction $Ln + Ln_2O_3 \rightarrow 3Ln^{3+}(e^-)O^{2-}$ is positive under normal conditions. But, as for the ionic monoxides, it does not preclude the preparation of metallic monoxides under other conditions and subsequent maintenance at ordinary pressure in a metastable state. In this reaction the 4f electron population is $4f^n$ in nearly all cases and the number of 4f electrons is conserved. ΔG° should then vary nearly smoothly across the rare earth series except for europium and ytterbium where the occurrence of two-electron metals raises ΔG° by about 84 and 42 kJ (16).

From Fig. 4, the standard Gibbs energy change of this reaction is given by

$$\Delta G^\circ = \Delta G^\circ_1 + \Delta G^\circ_2,$$

where ΔG°_1 corresponds to the formation of an ionic monoxide as calculated above and ΔG°_2 to the transformation of a saline monoxide into a metallic one. This latter process can be analyzed through the use of the thermodynamic cycle shown in Fig. 5, from which the following relation is obtained:

$$\Delta H^\circ_2 = 3U_2 + 3I'_3 - 3M + (27/2) \cdot RT$$

and

$$\Delta G^\circ_2 = \Delta H^\circ_2 - T\Delta S^\circ_2.$$

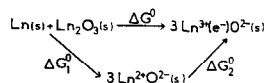


FIG. 4. Thermodynamic cycle for the formation of a metallic rare earth monoxide from metal and sesquioxide.

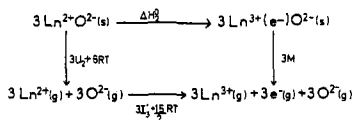


FIG. 5. Thermodynamic cycle for conversion of saline rare earth monoxides to a metallic state.

M is the dissociation energy of the metallic monoxide and the other quantities have their usual meanings.

During this process one electron per rare earth atom is delocalized through the condensed phase and a compound with metallic properties results. In this metallic phase the $5d$ electron participates in the bonding and when it is added to the two electrons per rare earth atom which are assigned to the anion in the ionic model, the total number of bonding electrons per rare earth is equal to 3. During the reaction the number of electrons in the $4f$ shell is reduced by one unit per mole (16) and it may therefore be expected that variations of ΔG°_2 along the rare earth series will be similar to those of the third ionization potential. ΔG°_2 cannot be calculated as no data for the lattice energy of the metallic monoxide are available but it is possible to evaluate ΔG°_2 for europium and ytterbium. Under a pressure of 300 kbar ionic europium monoxide transforms into a metallic phase with the same structure (26). The Gibbs energy change is the $P \cdot \Delta V_2$, where ΔV_2 is the volume difference between an ionic and a metallic monoxide, which can be calculated from Fig. 2 by interpolating the lattice parameters of metallic monoxides. ΔV_2 is then found to be $3 \text{ cm}^3/\text{mole}$ so $\Delta G^\circ_2 = +270 \text{ kJ}$.

The volume difference found experimentally (26) is smaller but it is not certain that the transition toward the $3+$ state is complete. In addition, ΔV_2 should not decrease markedly under pressure as the bulk modulus of EuO (1100 kbar) is close to those of trivalent oxides (1400 kbar) (27) and increases rapidly with pressure (26).

The volume difference ΔV_2 for ytterbium monoxide is found in the same way to be $2.3 \text{ cm}^3/\text{mole}$ and from the trend observed in chalcogenides (26) the transition pressure can be estimated to be about 200 kbar; a value of 138 kJ is then obtained for ΔG°_2 (YbO).

We now can calculate $\Delta G^\circ = \Delta G^\circ_1 + \Delta G^\circ_2$:

$$\text{Eu} \quad \Delta G^\circ = -140 + 270 = +130 \text{ kJ},$$

$$\text{Yb} \quad \Delta G^\circ = 0 + 138 = 138 \text{ kJ}.$$

The smooth ΔG° function is lower by 84 to 42 kJ for these two elements as stated previously, so it is higher for ytterbium than for europium. An increase of the ΔG° function with the atomic number is also found for the diiodides (16), for which no metallic compound is known for the heavier rare earth elements. This behavior of ΔG° appears to apply to the different rare earth systems, and if we combine it with the fact that for the monoxides ΔG° is always positive, we obtain the ΔG° function represented in Fig. 6. It shows that under normal conditions the lighter the rare earth, the closer to stability the trivalent rare earth monoxide.

The variation of the Gibbs energy change ΔG° for the reaction $\text{Ln} + \text{Ln}_2\text{O}_3 \rightarrow 3 \text{Ln}^{3+}$

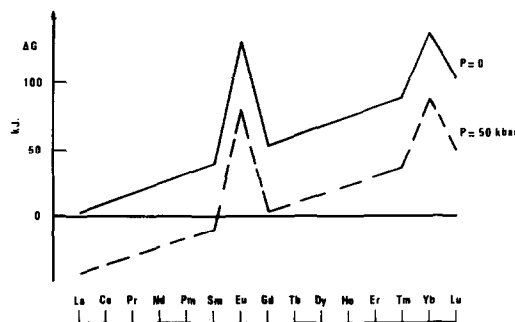


FIG. 6. Gibbs energy changes ΔG for the reaction $\text{Ln} + \text{Ln}_2\text{O}_3 \rightarrow 3 \text{Ln}^{3+}(\text{e}^-)\text{O}^{2-}$ at normal pressure and 50 kbar.

(e^-) O^{2-} is small and positive at normal pressure. When this reaction is performed under high pressure the value of ΔG° is modified by $P \cdot \Delta V$, where ΔV is the volume difference between the trivalent rare earth monoxide and the reactants. This volume difference ΔV is negative and roughly constant throughout the whole rare earth series. The effect of pressure is to reduce ΔG , which is positive under normal conditions. At a pressure of 50 kbar $P \cdot \Delta V$ is equal to -50 kJ (the volume difference should not be reduced by pressure as only trivalent rare earth oxides are considered) and it is then clear that ΔG becomes negative for the lighter rare earths but remains positive for the heavier ones (Fig. 6). The synthesis of trivalent rare earth monoxides, then, appears possible under high pressure for the lighter rare earth elements. This has been confirmed by the experimental results. We have been able to synthesize cerium monoxide at pressures as low as 15 kbar but pressures around 50 kbar were required to obtain samarium monoxide. We have not been able to obtain gadolinium monoxide at 50 kbar but it is quite likely that it should be obtained at higher pressures. These results support the evaluation of ΔG° . Once it is known ΔG°_2 can be obtained and the dissociation energy of the metallic monoxide M can be calculated:

$$M = U_2 + I'_3 + \frac{1}{3}[\Delta G^\circ_1 - \Delta G^\circ + \frac{27}{2}RT - T\Delta S^\circ_2].$$

The entropy term should be of the same order as that found in SmS, where a similar transition is observed. From the P-T diagram of SmS one obtains

$$T\Delta S^\circ_2 = T \frac{dP}{dT} \cdot \Delta V_2(\text{SmS}) \sim 0.4 \text{ kJ},$$

which is negligible. The value of M is much larger than the value of U_2 and varies smoothly in the rare earth series as expected.

IV. Conclusion

The standard Gibbs energy changes ΔG°_1 for the reactions $Ln + Ln_2O_3 \rightarrow 3 Ln^{2+}O^{2-}$ have been calculated. As expected it shows that $Eu^{2+}O^{2-}$ should be stable; $Yb^{2+}O^{2-}$ appears to be on the stability border. Under high pressures the values of ΔG°_1 are lowered, but appreciably only in the case of $Yb^{2+}O^{2-}$ (leaving aside $Eu^{2+}O^{2-}$), which explains its synthesis under these conditions.

The standard Gibbs energy changes ΔG° for the reactions $Ln + Ln_2O_3 \rightarrow 3 Ln^{3+}(e^-)O^{2-}$ have been evaluated; they are found to be small and positive and to increase with the atomic number of the rare earth. Under a pressure of 50 kbar, ΔG° is sufficiently lowered to make possible the synthesis of metallic monoxides of the lighter rare earths.

The rare earth monoxides have the fcc structure, like the monochalcogenides. The cell parameters decrease regularly along the series according to the well-known lanthanide contraction. Two major exceptions are europium and ytterbium, for which the larger cell parameters are due to the divalent state of the rare earth which is confirmed by the magnetic properties (20). Moreover for europium and ytterbium (20) and intermediate oxide Ln_3O_4 , ($Ln^{2+}O$, $Ln^{3+}_2O_3$) exists between LnO and Ln_2O_3 ; its structure is orthorhombic. No such oxide is found for the other rare earths. In the remaining monoxides, except for SmO, the rare earth is in the trivalent state. This is shown by the metallic properties (low resistivity $\sim 300 \mu\Omega \cdot \text{cm}$) and the magnetic susceptibilities (25) which are characteristic of trivalent rare earth ions.

The case of samarium is more complex: the cell parameter is only slightly larger than the value calculated for a trivalent samarium monoxide. From the observed value of the cell parameter it is deduced from Vegard's law that samarium is in an

intermediate valence state (2.9) close to 3 since all the samarium sites are crystallographically equivalent. This anomalous valence state is also confirmed by magnetic susceptibility measurements and XPS data (25). So the properties of SmO are very similar to those found for the high-pressure phase of SmS which is isoelectronic and isostructural with samarium monoxide.

The rare earth monoxides offer a unique series where a large variety of properties are displayed at normal pressure: they go from normal trivalent rare earth monoxides (LaO, CeO, PrO, NdO) which are metallic to divalent rare earth monoxides (EuO, YbO) which are semiconductors passing through an intermediate valence samarium monoxide which is metallic but shows unusual magnetic properties. Further study of this compound, which is stable under normal conditions, should allow us to understand better the intermediate valence state phenomena without using systems perturbed by different electronic configurations resulting from the addition of a third component and without the limitations imposed by *in situ* measurements at high pressure as for SmS.

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