non-comparable group steps. The former may be second-order – provided that Landau theory authorizes it – while the latter are obligatory first-order. Contrary to a generally accepted opinion, it can be seen that here the symmetry does not necessarily decrease when the temperature is lowered.

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On 'non-stoichiometric phases' in thin films of rare-earth oxides.

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Kaul & Saxena [*Acta Cryst.* (1977), A33, 992–996] have reported the existence of long-range and short-range order in a non-stoichiometric phase 'LnO_x' (Ln = rare earth). It is shown that the experiments they are describing are indeed the oxidation of the rare-earth hydride LnH_2 into the rare-earth cubic *C*-type sesquioxide. The interpretation they give of their experiments is to be discarded entirely.

Kaul & Saxena (1977) recently published a paper on rare-earth metal-oxide thin crystals which contains an interpretation of the experimental data considerably at variance with the results of other workers in this field. Some of the interpretations suggested for the chemical composition of the thin films and for the diffraction data have been published before and have been criticized by several teams of investigators (Gasgnier, Ghys, Schiffmacher, Henry la Blanchetais, Caro & Boulesteix, 1974; Gasgnier, Henry la Blanchetais & Caro, 1976; Curzon & Singh, 1975*a*,*b*, 1977*a*,*b*; Surplice, 1976; Cadim & Al-Bassam, 1977; Safrai, Buckwald & Hirsch, 1976). We should like to point out once again some of the errors involved.

The stability of rare-earth monoxides in the solid state

Kaul & Saxena (1977) suggest the existence in thin films of the monoxide 'LnO' (Ln = rare earth) as a f.c.c. phase. They claim that this material is 'reasonably well understood'. They give as evidence the old paper by Eick, Baenziger & Eyring (1956) but they choose to ignore more recent papers of two of these authors (Felmlee & Eyring, 1968; Work & Eick, 1972), which criticize their first paper, and they also ignore the work of McCarthy & White (1970) as well as that of Brauer, Bärnighausen & Schultz (1967).

Felmlee & Eyring (1968) have shown that for Sm the compounds called 'SmO' and '$\mathrm{Sm_2O}$' are in fact $\mathrm{SmN}_{1-x}\mathrm{O}_x$ and SmH_2 respectively, and that the cation is always in the trivalent state.

Work & Eick (1972) have shown that it is thermodynamically impossible to prepare 'ScO' and that the material elaborated by Dufeck, Bronzek & Petrie (1969) is, in fact, an oxynitride $\mathrm{ScO}_x\mathrm{N}_y$.

McCarthy & White were unable to prepare 'SmO' by oxidation–reduction (the technique for the preparation of EuO). They describe several unsuccessful attempts to obtain the monoxide. Brauer *et al.* (1967) have shown that it is impossible to obtain 'SmO' by reaction of the metal with the sesquioxide.

It is well known from the work of Johnson (1969) that the reducibility order of the rare earths is: Eu, Yb, Sm, Tm, Pm, Dy, Nd, Ho, Er, Pr, Tb, Ce, Gd and La. It is possible to obtain divalent cations down to Nd in halide systems but in chemical systems involving O, it is possible to reduce only Eu^{3+} and possibly Yb^{3+}.

Kaul & Saxena (1977) suggest that their 'LnO_x' f.c.c. phase may also have a value of x larger than 1·5 tending to the LnO_2, CaF_2-type phase. Such a phase is known only for Ln = Ce, Pr, Tb (Kunzmann & Eyring, 1975) and for the last two rare earths this phase is stable only at a high pressure of oxygen. It is highly improbable, if not completely impossible, that a phase with $x > 1{\cdot}5$, especially for Er and Dy, will be prepared under a 10^{-6} torr vacuum.

The f.c.c. phase

Kaul & Saxena (1977) claim, after several of their co-workers and Semiletov, Imanov & Ragimli (1974, 1976), that in thin films the 'LnO' phase exhibits an f.c.c. electron diffraction pattern. They add that 'the oxygen content in these oxide films may be large, and therefore, although the oxides are f.c.c., they are not quite like *R*O (*R* = rare earth) which has the ZnS-type structure, but are RO_x type with $1 < x < 2$ and tend to have a structure approaching that of CaF_2'. It has been shown by Gasgnier *et al.* (1974, 1976), Surplice (1976), Müller, Singh & Surplice (1972), Curzon & Singh (1975*a*,*b*, 1977*a*,*b*), Holloway & Swartz (1977) and Cadim & Al-Bassam (1977) that the f.c.c. phase is the hydride LnH_2 which indeed has a CaF_2 structure.

Kaul & Saxena (1977) say that the thin films were prepared by 'vacuum evaporation of Er_2O_3 and Dy_2O_3 powder (99·9% pure) on copper supporting grids in a vacuum of about 10^{-6} torr'. It is well known that rare-earth oxides are highly refractory materials very difficult to vaporize. It is well known also that they can be reduced in vacuum by metals with a high affinity for oxygen, or having volatile oxides. The *metal* formed will then efficiently getter the residual hydrogen and the residual water vapour within the vacuum chamber (Dexpert-Ghys, Loier, Henry la Blanchetais & Caro, 1975; Gasgnier *et al.*, 1974).

The behaviour of the f.c.c. phase under pulse annealing

When the f.c.c. phase (LnH_2) is heated within the electron microscope by pulse annealing it is oxidized to the rare-earth sesquioxide by gettering of the residual oxygen in the microscope. In the case of Er and Dy the b.c.c. *C*-type sesquioxide would be obtained. As the transformation proceeds the two phases usually have an epitaxic relationship (Gasgnier *et al.*, 1974, 1976). Murr (1967) and Curzon & Chlebek (1973*a*,*b*,*c*) have also observed the formation of the *C*-type sesquioxide by pulse annealing of Er and Dy thin films. At that time the initial state was interpreted as being 'ErO' + Er h.c. by Murr and as 'Er or Dy f.c.c.' by Curzon & Chlebeck. The parameters reported for 'ErO' and Er or Dy 'f.c.c.' were always close to those of ErH_2 and DyH_2. Later, Curzon & Singh (1975*a*,*b*) recognized that their initial conclusions about the chemical nature of the 'f.c.c.' structure were erroneous and they stated that their 'new phase' was in fact the dihydride. For Murr as well as for Curzon & Chlebek the final state after light or strong annealing is identical in both cases. Their observations by electron microscopy and diffraction are similar to those of Boulesteix, Pardo, Gasgnier, Henry la Blanchetais & Caro (1974) and Gasgnier *et al.* (1974). Kaul & Saxena (1977) interpret the phenomena during the oxidation of the hydride as being due to a loss of oxygen from their samples. Although the data described are correct, their interpretation is entirely false. To test the validity of their hypothesis these authors can use a simple procedure: *i.e.* oxidize their initial samples to the sesquioxide by heating them in air and note whether the weight increases or decreases. Curzon & Chlebek (1973*b*) have done this in the case of Er, with the same initial material (lattice parameter a = 5·09 Å) as that described by Kaul & Saxena (1977). They found a weight increase which contradicts the hypothesis of Kaul & Saxena (1977) who claim that 'the starting material for the preparation of thin films was Ln_2O_3, and thermal evaporation may lead to the incorporation of additional oxygen leading to the formation of LnO_x ($x > 1{\cdot}5$)'.

These authors realize that their final diffraction patterns have roughly the same parameters as the *C*-Ln_2O_3 phase; hence, to uphold their idea of oxygen loss, they assume that their former 'LnO_x' phase with $x = 1$ is indeed in their present preparation an 'LnO_x' phase with x close to 2, of the CaF_2 type. They further claim that they obtain a different structure which they call 'long-range order' because they observe the 110 spots 'forbidden' within the space group T_h^7 of *C*-Ln_2O_3. These spots are forbidden only within the framework of the kinematical theory of electron diffraction. These spots do appear in normal *C*-Ln_2O_3, either as thin films or in the bulk form (Boulesteix *et al.*, 1974) and this can be easily explained within the framework of the dynamical theory of electron diffraction (Pardo & Zogheib, 1974). Curzon & Chlebek (1973*c*) and Murr (1972) concluded that the real space group of *C*-Ln_2O_3 was T_h^7 (*Ia*3) and not T^5 (12_13) as suggested previously by Murr (1967). For these authors the phenomenon of the appearance of the forbidden reflections was a simple mechanism of double diffraction.

Besides, we can recall that Boulesteix *et al.* (1974) have shown that a small thin single crystal of Y_2O_3, obtained by crushing an oxide melted in a solar furnace, presents a diffraction pattern identical to that given in Fig. 9 of Kaul & Saxena (1977) (zone axis [111]). Also, by tilting the sample a new diffraction pattern is observed without forbidden reflections in the zone axis [001].

Tsutsumi (1970) has prepared Y_2O_3 thin films by electron-gun evaporation (the source temperature was about 2500°C). By X-ray diffraction and electron diffraction he shows that the lattice constant is that of the bulk material. He notes that no suboxide is present.

Gasgnier (1975) studied Tl_2O_3 thin films by oxidation of Tl metal thin films. Identical diffraction patterns are observed for this oxide and for *C*-Ln_2O_3. These two sesquioxides have the same space group in the bulk state.

Now we should like to point out the possible effects of a change in the microscope constant. We have examined the same sample in three different microscopes. The variations owing to focus, to non-planarity of the grid, to the effects of ellipticity and above all to the heating of the column and of the microscope elements in the course of the thermal treatment (pulse annealing or regular heating) of the sample can lead to differences in the range of 1 to 4% (of the value of the microscope constant). The best method for a precise calibration (accuracy better than 0·5%) is to evaporate a well known material (such as Al or Ag) as a very thin film directly on the sample.

In their experimental procedure Kaul & Saxena (1977) make no mention of this accurate calibration technique; for instance, their diffraction patterns (Figs. 9 and 10) present two reciprocal-lattice sections with an identical interreticular distance (the {110}-type spots). If there is no change in the magnitude by reproduction, the calculated microscope constants are respectively 5·78 (Fig. 9) and 5·50 (Fig. 10).

The lattice parameters determined by Kaul & Saxena (1977) do not agree with those of the bulk state or with those of Murr (1967) and Curzon & Chlebek (1973*a*) obtained on annealed samples. Consequently, the accuracy of their measurements is automatically called into question regardless of how they choose to obtain the microscope constant.

Finally, we note that Kaul & Saxena (1977) give for the a cubic parameters of their phases the values $a_{Er_2O_3} = 10{\cdot}41$ Å and $a_{Dy_2O_3} = 10{\cdot}18$ Å; this contradicts the classical lanthanide contraction law. They have not verified this surprising result by X-ray diffraction.

Conclusion

The interpretation of their observations given by Kaul & Saxena (1977) is, in our opinion, to be dismissed entirely. The experiments reported correspond to the oxidation of the hydride LnH_2 (Ln = Dy, Er) into the *C*-type sesquioxide Ln_2O_3 (Ln = Dy, Er). They ignore the high gettering power of rare-earth-metal thin films, which causes the formation of chemical compounds other than the oxides.

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Determination of electronic polarizabilities of ions in orthosilicates.

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Electronic polarizabilities of cations have been obtained for the sodium *D* line (in Å^3): Mg^{2+} 0·1, Fe^{2+} 3·3, Zn^{2+} 5·4, Zr^{4+} 4·6. The polarizability of the O^{2-} ion varies from one structure to another. It has been shown that calculation of electronic polarizability is possible only if an accurate structure refinement is available.

Recently, a method of determining electronic polarizabilities of ions in crystals has been given by Pohl (1978). If both optical and structural data are available, polarizabilities can be obtained for the ions composing the structure of a doubly refracting crystal. This method has been applied to orthosilicates containing just one type of cation: Be_2SiO_4, Mg_2SiO_4, Fe_2SiO_4, Zn_2SiO_4 and $ZrSiO_4$. In applying the method, it is assumed that the polarizability of the Si^{4+} ion is negligible compared to that of the other ions. Since this assumption does not hold for Be_2SiO_4, this compound was assumed to contain only one type of polarizable ion, namely O^{2-}. Refractive indices were obtained from the compilation by Winchell & Winchell (1964). On the basis of recent structural data (see references in Table 1) electronic polarizability values for λ = 5893 Å (sodium *D* line) were computed. The results are given in Table 1. For comparison,