

## CRYSTAL STRUCTURES BONDS AND RELIANCE IN MX\*

(M = La, Ce ... Yb and Sc, Ti ... Zn; X = S, Se, Te)

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Large variations of the molecular volume of the monochalcogenides of rare earths are attributed to cation-cation bond which involves one deep valence electron. Similar results are found with monochalcogenides of 3d metals. The phase transformation  $Cey \rightleftharpoons Ce\alpha$  is interpreted in a similar way bearing in mind the existence of compounds such as  $XeF_4$ . This work introduces the notion of reliance which enlightens the notion of valence and is closely related, to the notion of intermediate and fluctuating valences.

## 1. INTRODUCTION

Cerium metal or SmS exhibit very interesting phase transformation. With the same crystal structure there is a large variation in the lattice parameters<sup>1,2</sup>. In order to interpret these properties, a change of valence was supposed eventually together with fractional valence giving the notions of valence instabilities and intermediate valences. But these notions have not led to a clear solution of the problems. In our opinion one of the difficulties is that we must distinguish between two aspects. On the one hand the existence of bonds each involving one electron and on the other hand the strength of each bond. Shrinkage with large variations in the molecular

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or atomic volume must be attributed at least to one new bond involving the participation of one electron. Small variations in volume must be explained by variations in the intensity of the bonds.

From this view, the study of the monochalcogenides of the rare earths ( $\text{LnX}$ ) is very interesting. In most of these compounds, together with their oxidation number two leading to two bonds of an ionic type, exists one cation-cation bond leading to the notion of reliance: the total number of bonds. This first study will be related to the case of monochalcogenides of the  $3d$  metals and finally to the study of the phase transformation  $\text{Ce}\gamma \rightleftharpoons \text{Ce}\alpha$  with the help of the chemical properties of xenon. A preliminary version of this work has been published already<sup>3</sup>.

## 2. THE MONOCHALCOGENIDES OF RARE EARTHS

All the monochalcogenides of rare earths crystalize at low pressure forming NaC structure. However, in spite of this structural homogeneity, according to either the variation in their lattice constant (Fig. 1) or to their electrical conductivity, and their magnetic susceptibility, they can be divided into two groups<sup>4-12</sup>.

Let us consider the group with a higher lattice parameter; it contains the monochalcogenides of barium, a metal known to give compounds essentially with the loss of its two  $6s$  electrons. This group equally contains monochalcogenides of ytterbium, europium and samarium, elements known to give relatively easily compounds in which they have just lost their two outer  $6s$  electrons and without any interaction with a third electron. We have there elements, the oxidation number (o.n.) of which is II, bound to the anion through two ionic bonds. The ions to be considered are  $\text{Ba}^{2+}$ ,  $\text{Ln}^{2+}$ ,  $\text{S}^{2-}$ ,  $\text{Se}^{2-}$  and  $\text{Te}^{2-}$ .

Then what makes the other monochalcogenides different? In fact this group, by the shrinkage of the lattice constant, reflects an existence of an additional bond causing this shrinkage. Then which electron is responsible for this bond? The one which out of the two  $6s$  allows the formation of the sesquioxide  $\text{Ln}_2\text{O}_3$ . The Curie constant value of the monochalcogenides allows us to make such a presumption. This bond would not concern the anions that have an electronic configuration of rare gases. Thus, the bond arises between cations of the same element. In fact, this is expressed in a different way by the current models. In this model, the electron initially at  $4f$  level goes to the  $5d$  level where it contributes to a conduction band with all the other similar electrons from the other Ln ions. To suppose that the electrons make a band is to suppose that their ions interact, which is another way of speaking about a cation-cation bond. Moreover, these electrons have at the same time their magnetic contribution quenched as shown by the Curie constant. Thus, as a matter of habit, people speak of the  $\text{Ln}^{3+}$  ion, in a language that wants to emphasize the properties that we have just recalled. In another respect, the notion of ionic radius is directing people in this way. We have to use the radius of the ion

$\text{Ln}^{3+}$  with those of the corresponding chalcogen ion  $\text{X}^{2-}$  to explain the lattice parameters of these compounds<sup>4</sup>. This fact has led to speak about the monochalcogenides as of trivalent rare earths. In such use of language, there is some uncertainty that is desirable to remove, especially from the view of this analysis in the case of  $3d$  metals. Thus, instead of speaking of valency three we shall underline the existence of a cation-cation bond. In order to do this, let us note that if the electrons implied in a cation-cation bond give to the crystal its metallic character, whatever is their delocalization in a band, on an average there is one per cation. As a result, the average charge for a cation is  $2+$ , and it is balanced with the charge  $2-$  of the anion. Thus, we have a rare earth cation with a charge plus two, which contributes to two ionic bonds.

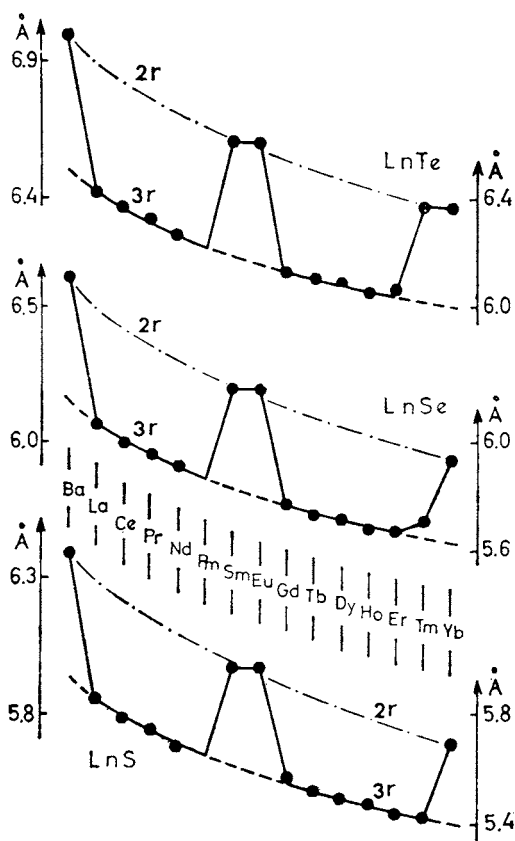


FIG. 1

The lattice constant (refs<sup>4-12</sup>) of rare earth and barium monochalcogenides.  $2r$  or  $3r$  according to the reliance, see the text.  $1\text{Å} = 1 \cdot 10^2 \text{ pm}$

When taking into account the binding properties of the cation, it is not sufficient just to consider these two bonds. Let us call the reliance the number of bonds: the two ionic bonds and the cation–cation bond<sup>3,13</sup>. In this case the reliance is three. Then, let us adopt the notation  $\text{Ln}(2+, \text{II}, 3r)$ : the Arabic numeral for the ionicity, the Roman numeral for the o.n. and  $3r$  for the reliance. In the past I had adopted another form of notation but it appears useful to introduce a clear distinction between the oxidation numbers and the total number of bonds – the reliance<sup>3</sup>. The necessity of a distinction between the ionicity and oxidation number comes from a discussion of the  $\text{La}_2\text{O}_3$  and spinel crystal structure<sup>3,13</sup>. Now, when there is no cation–cation bond we have reliance two and  $\text{Ln}(2+, \text{II}, 2r)$ . We shall also write that as  $\text{Ln}^{2+}$ , thus the reliances  $2r$  and  $3r$  are each characteristic of one of the two groups of the monochalcogenides of the rare earths, so we used them as label in Fig. 1.

It is noteworthy that the cation–cation bond giving the reliance  $3r$  does not modify the o.n. which remains II. These are two important characteristics to apprehend solid state properties.

### 3. VOLUME AND BONDS

The rare earths separation was for a long time extremely difficult. This difficulty comes from the great homogeneity of their chemical properties. First of all, these elements have the oxidation number III and, for example, possess very easily the sesquioxide  $\text{Ln}_2\text{O}_3$ , the other type of combination being more difficult to stabilize. As a result, in the study of a family like  $\text{LnX}$ , going from one element to the next following according to the increasing atomic number, we can study the variation in volume or in the lattice parameter which follows from the shrinkage of the atom arising from the increasing charge of the nucleus. As we are dealing with a very large family of fourteen elements from La to Yb, if a small number among these fourteen exhibits a different behaviour, it is very prominent. It is exactly the case of Sm, Eu and Yb in the three families of  $\text{LnX}$  in respect to the others, this fact being well exhibited again by the adjunction of barium. Hence, as regards the volume of the compounds in the case of the rare earth elements we have the possibility of separating this into two; one which arises from the specific atomic volume and the other due to interatomic interactions, or in other words to the bonds between atoms.

Now, let us consider the  $3d$  transition metals with the great variety in chemical properties that has allowed their separation for a long time. This variability arises from the fact that each additional electron in the shell  $nd$  brings a new possibility of bond formation, at least up to the fifth  $d$  electron. Therefore, it is not the great homogeneity showing slow variation in the molecular volume or in the lattice parameter which take place advancing from one element to the next in the succession of the atomic numbers within the same family, but rather the large variations reflecting ionic, as well as the covalent bonds. Moreover, if we add that transition metals are

ten rather than fourteen, we shall understand that the studies of the variations in volumes of the monochalcogenides of the transition metals have not taken into view the knowledge that the  $\text{LnX}$  has just brought to us.

#### 4. THE MONOCHALCOGENIDES OF 3d METALS

The study of the monochalcogenides of 3d metals which we shall write as  $\text{MX}$ , appears as a different type from that of the rare earth metals. The first difference comes from the variety of the crystal structures<sup>5</sup>, six for  $\text{MX}$  to one for  $\text{LnX}$ . The second difference is that up to the manganese, for each extra electron existing for the element, there are compounds in which this electron is involved in a bond. Thus, this element can have one extra unit of o.n. This aspect is illustrated, for example, by the oxides  $\text{CaO}$ ,  $\text{Sc}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{V}_2\text{O}_5$ ,  $\text{CrO}_3$  and  $\text{Mn}_2\text{O}_7$ .

From the point of view of the electrical properties, many of those compounds which crystallize with the structure of  $\text{NiAs}$  or a close structure are metal like<sup>14</sup>. Results indicate the existence of band, hence of cation-cation bonds. However, some exhibit an insulator-metal transition, for example  $\text{NiS}$ ,  $\text{FeS}^{15-17}$ , and as a result, the electrical conductivity cannot serve as a guide as in the case of  $\text{LnX}$ . The same refers to the magnetism. The Curie constants of  $\text{FeS}$  and  $\text{MnS}$ , for example, correspond to that expected for an o.n. II. Even if some other compounds can lead to a presumption of an o.n. higher than two, here again the Curie constant cannot serve as a guide in this search.

##### 4.1. A BOND SCALE

To document the existence of the two families of  $\text{LnX}$  we have mostly compared the lattice parameters. This was possible because all these compounds crystallize in the  $\text{NaCl}$  structure. However, in the case of  $\text{MX}$  due to different crystal structures it is necessary to compare the molecular volumes and not just lattice parameters. The molecular volume is defined as the volume of the cell divided by the number of molecule per cell. Therefore, the aim is to know what is the influence of the structure upon the molecular volume. The  $\text{LnX}$  have led us to discover the importance of the contribution of a bond in the same structure. Then the hypothesis is suggested that the molecular volume is determined rather by the number of bonds than by the structure itself. Let us consider, for example, the structures  $\text{NiAs}$  and  $\text{NaCl}$  where the anions are in a hexagonal closed packed (h.c.p.) and cubic closed packed (f.c.c.) arrangements, respectively. This represents two closed packed arrangements where the cations are at octahedral sites. The role of the structure remains weak as long as the number of electrons implied in a bond is the same. The case of the selenides of manganese corroborate this hypothesis well. For two of them, one has the crystal structure of  $\text{NaCl}$  and its molecular volume is  $40.43 \cdot 10^6 \text{ pm}^3$ , the other has the

crystal structure of NiAs and its molecular volume is  $40.22 \cdot 10^6 \text{ pm}^3$ . The case of the monochalcogenides of scandium, which are either of the type NaCl or NiAs (ref.<sup>18</sup>), will show us the crucial role of the number of bonds in respect to the structure concerning the determination of the molecular volume.

In NaCl and NiAs structures the cations occupy the octahedral site and in ZnO and ZnS structures they occupy the tetrahedral sites, the anions having f.c.c. and h.c.p. arrangement, respectively. We shall suppose similarly that the octahedral or tetrahedral surroundings of the cation have just a secondary role in respect to that of the bonds for the determination of the molecular volume. Let us presume that it applies again to the sulfides and selenides of copper which are not easily linked to the previous ones, and also for the telluride of copper which has its own crystal structure. Only an analysis of each case and the coherency of the ensemble will prove the posterior validity of this approach.

#### *Calcium and Zinc Monochalcogenides*

Now, let us consider the variations in the molecular volumes of the MX as a function of the atomic number plotted in Fig. 2. Calcium and zinc are known to possess just two 4s electrons as bond electrons. Thus, the respective molecular volumes of their monochalcogenides locate those having two bounds. Thus, we see a first comparison between the molecular volume of MX having NaCl structure on the one hand and those having the structure of ZnS and ZnO on the other hand, in cases where we can suppose that there are just two electrons involved. The volume variation from one monochalcogenide of calcium to its homologues of zinc is of the order of a magnitude of 15%. It is mostly the result of the increasing charge of the nucleus with a small part due to the structure, and from one atomic number to the next the variation per unit charge is 1.5%; the case of the scandium shows more important variations. Let us note that in the cases of CaX and ZnX the reliance is  $2r$ , measured with the same number as the o.n. II or the ionicity for the absolute value. The cation can be written  $M(2+, II, 2r)$ , but in a more simple way as usual  $M^{2+}$ .

#### *Scandium Monochalcogenides*

Let us now consider the case of ScX (ref.<sup>18</sup>). Scandium has just its three electrons  $4s^2$  and  $3d^1$  which contribute to bonds. Going from CaX to its homologue ScX we note a strong shrinkage of the molecular volume. Thus, the molecular volume of the ScX locates among those having three bonds, that is two ionic bonds and one cation-cation bond, as in the case of the LnX. So as to be well ensured that we are concerned with the same phenomenon as that one exhibited by LnX, we have to plot the representative points of the molecular volume of LaX modifying the scale of Fig. 2 in such a way that BaX have their representative points at the same places as those of CaX. The representative points of LaTe and ScTe-LaSe and ScSe-LaS and ScS are

then almost at the same place justifying the three bonds attributed to the scandium in its different monochalcogenides. Then the reliance is  $3r$  and we have  $\text{Sc}(2+, \text{II}, 3r)$ . Let us note in passing that  $\text{ScTe}$  crystallizes in  $\text{NiAs}$  structure and  $\text{ScSe}$  and  $\text{ScS}$  in  $\text{NaCl}$  structure. Thus, the case of  $\text{ScX}$  establishes well for the molecular volume the negligible influence of the structure as compared to that of the bonds.

### Titanium Monochalcogenides

Now, we concentrate at the case of  $\text{TiX}$ . The titanium with two  $4s$  and  $3d$  electrons can have four bonds. We note with  $\text{TiX}$  a further important shrinkage of their molecular volume as compared to that of their homologues  $\text{ScX}$ . An idea of the order of magnitude can be gained from the ratio of the molecular volume of  $\text{TiTe}$  to that of

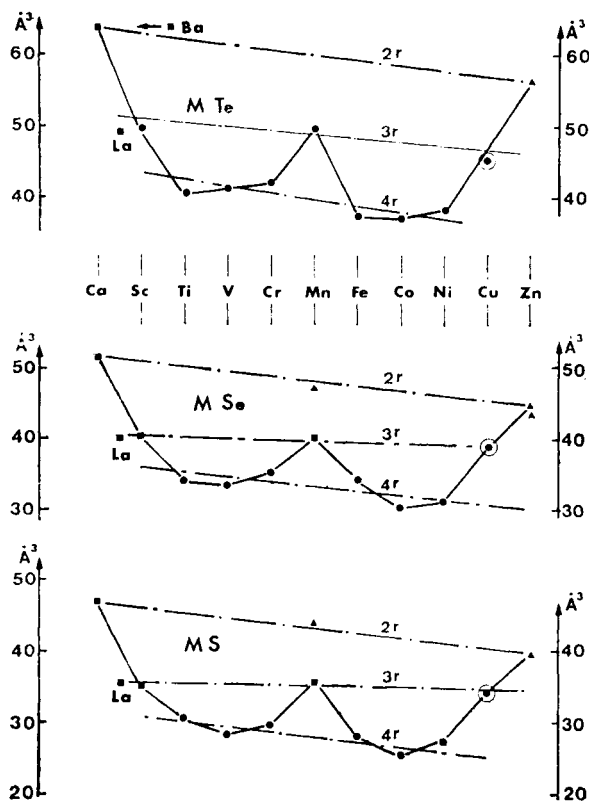


FIG. 2

The molecular volume of the monochalcogenides of the  $3d$  transition metals. The circle around the representative point of the  $\text{CuX}$  recall that they have their own structures.  $2r$ ,  $3r$  or  $4r$  according to the reliance. Structures  $\blacksquare$   $\text{NaCl}$ ,  $\bullet$   $\text{NiAs}$ ,  $\blacktriangle$   $\text{ZnS}$  or  $\text{ZnO}$ .  $1 \text{ Å}^3 = 1 \cdot 10^6 \text{ pm}^3$

CaTe, which is 0.64, namely a variation of 36%, whereas the ratio of the molecular volume of ScTe to that of CaTe is 0.78, namely a variation of 22%. The ratios are very nearly the same for the sulfides and the selenides. These numbers then demonstrate that with the monochalcogenides of titanium there is additional bond as compared to those of scandium. It is then two cation-cation bonds that we have to consider in addition to the two ionic bonds that is a reliance of  $4r$  and cations we write in the form  $Ti(2+, II, 4r)$ . The  $TiX$  represent then the molecular volume of monochalcogenides having four bonds that is with a reliance  $4r$ .

#### *Vanadium, Chromium, Iron, Cobalt, and Nickel Monochalcogenides*

According to these four cases:  $CaX$ ,  $ZnX$ ,  $ScX$  and  $TiX$  now we can classify all the other molecular volumes. Let us first consider the monochalcogenides of vanadium, chromium, iron, cobalt and nickel. With respect to their homologues of titanium, they do not exhibit a large variation of the molecular volume. Then we can suppose that they all have two cation-cation bonds in addition to the two ionic bonds corresponding to their two  $4s$  electrons, so the reliance is  $4r$ , and their ions can be noted  $M(2+, II, 4r)$ . In Fig. 2, we have presented three lines denoting  $4r$ ; all the  $MX$  having such four bonds have their representative points of their molecular volume in the vicinity of the corresponding one. Let us emphasize that all these compounds crystallize with the NiAs structure.

#### *Manganese and Copper Monochalcogenides*

Let us now consider among the monochalcogenides of manganese, those which crystallize in NaCl or NiAs structure<sup>5,19</sup>. Their molecular volumes are similar to those of the monochalcogenides of scandium. The same holds for that of copper. It is possible to verify that for the sulfides, selenides and tellurides of these three elements the representative points of their molecular volumes are in the vicinity of the same line that we have denoted as  $3r$ . Indeed, we can consider for those compounds that there is one cation-cation bond in addition to the two ionic bonds as for the scandium. The reliance of the cations is  $3r$  and they can be noted  $M(2+, II, 3r)$ .

We are left to consider the sulfides and selenides of manganese which crystallize in either ZnS or ZnO structures. They fall in the vicinity of the line which joins their homologues of calcium and zinc denoted by  $2r$ . In Fig. 2, there is just one representative point for the sulfides and another for the selenides, because the respective volumes corresponding to the two kinds of structure are almost at the same place. The logic followed in this analysis leads to suppose that these sulfides and selenides of manganese have only two bonds of ionic type and nothing else. These monochalcogenides of manganese have a larger molecular volume than their homologues which crystallize in the NaCl structure, therefore we have assumed an additional cation-cation bond.



One can think that the difference in volumes comes from the difference of cation site: octahedral for the NaCl structure and tetrahedral for the two other structures. A difficulty arises that one must not ignore. We have to note that the molecular volumes of the MnX with ZnS or ZnO structures are of the same magnitude as of their homologues of zinc. Finally, let us note that Wyckoff<sup>5</sup> refers a telluride of manganese having the ZnO structure with a molecular volume very near to that having the NiAs structure and in which there is a cation-cation bond to consider. Whatever the reason, the essential of the results concerns the structures NaCl and NiAs for which there is no difficulty occurring. Taking the case of ZnX it seems possible to extend this analysis to the MnX having this structure. As regards the CuX, they cannot be compared by means of their structures: according to their molecular volumes they belong to the same case as ScX. In conclusion, let us recall that the cation-cation bonds have been proposed already to explain the electrical and magnetic properties of different oxides<sup>20-23</sup>.

#### 4.2. BONDS AND IONIC RADII

Thus, in the monochalcogenides of 3d transition metals, we have cations with ionicity 2+ and also one or two cation-cation bonds that we refer to as M(2+, II, 3r) and M(2+, II, 4r). As we have recalled in the study of LnX, one of the interests of Iandelli's work<sup>4</sup> is to show how the rare earth ionic radii corresponding to the o.n. III give a good evidence of the cation-anion distances. Then the question is to know if this is again the case with MX. We know that where the metal due to its chemical combinations has three or four electrons implied in a bond as with the oxides M<sub>2</sub>O<sub>3</sub> or MO<sub>2</sub> the system of ionic radii gives a good evidence of the cation-anion distances. We shall see that generally those same ionic radii of oxidation number III or IV also give a good measure of the cation-anion distances in MX when the cations with reliance 3r or 4r can be considered. For this purpose we have calculated two distances. One  $\delta_m$  calculated from the lattice constants, the other  $\delta_r$  which is the sum of the radii of the cation  $r_c$  and of the anion  $r_a$ . The results are presented in Fig. 3. To avoid any ambiguity about the more or less important ionic character of some ions, we indicate the oxidation number of the cation by the corresponding Roman numeral associated with the chemical symbol in place of the ionicity. Thus, we do not use the notation Fe<sup>3+</sup>, Ti<sup>4+</sup> but Fe<sup>III</sup> or Ti<sup>IV</sup>.

For the usual oxidation number, the ionic radii used for the comparison in Fig. 3 are those given by Wyckoff<sup>24</sup>. In choosing a set of ionic radii, those of cations are generally defined in 6-fold coordination with respect to oxygen. We are concerned with the neighbour which is either sulphur, selenium or still tellurium. But with the same charges, the size of the anion modifies the coulombic interaction. Thus, the radius of the cation is modified. This point is discussed in more detail in ref.<sup>3</sup>.

The comparison between  $\delta_m$  and  $\delta_r$  is given in Fig. 3. In this comparison we consider only the NaCl and NiAs structures. In this way all the cations occupy octahedral sites so that the results are comparable from one element to the next. This is the reason for which the cases of the zinc and manganese monochalcogenides with ZnS or ZnO structures are not dealt with. The same accounts for the sulfide, selenide and telluride of copper, the structures of which have no octahedral site. Finally, in the structure of NiAs the cation is slightly out off the centre of the octahedral site. This divergence is not known generally, so  $\delta_m$  has been calculated as if there is no divergence.

What are then the results which become apparent from this comparison? For the sulfides, selenides and tellurides of scandium the radius of the  $\text{Sc}^{\text{III}}$  ion gives a good measure of the distances  $\delta_m$ . The three bonds attributed to the scandium are then corroborated well. It is the same for the four bonds attributed to titanium or vanadium in their three monochalcogenides. Indeed, the calculation of  $\delta_r$  uses the radii of the ion  $\text{Ti}^{\text{IV}}$  or  $\text{V}^{\text{IV}}$ .

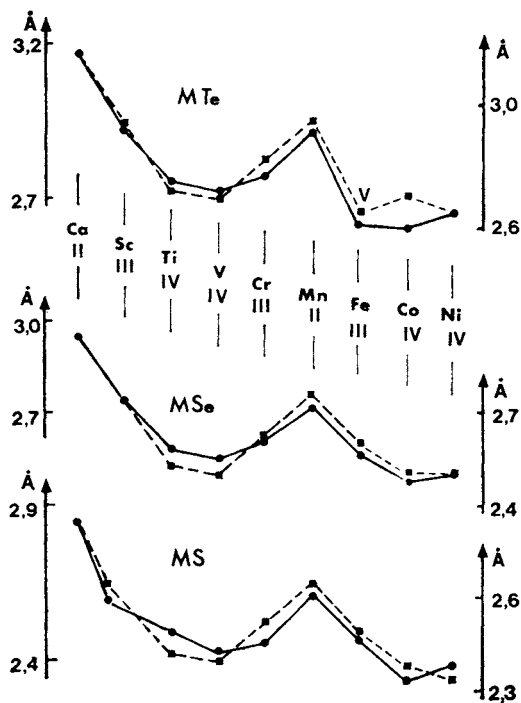


FIG. 3

Comparison of the distance  $\delta_m$  ——— and  $\delta_r$  - - - -. The oxidation number of the considered ion is indicated by the Roman numeral, except for  $\text{Fe}^{\text{V}}$  in  $\text{FeTe}$ . Cation-anion distance —●—●—, cation-anion radii —■—■—

The other compounds MX exhibit a different situation. For those of chromium it is the radius of the  $\text{Cr}^{\text{III}}$  ion which accounts for  $\delta_m$ . For the compounds  $\text{MnX}$  with the structure of NiAs or NaCl it is the radius of the ions  $\text{Mn}^{\text{II}}$  which accounts for  $\delta_m$ . For FeS and FeSe the situation is the same as for the three CrX. With the compounds FeTe, CoX and NiX, to ascertain the cation-anion distance  $\delta_m$  one has to introduce ionic radii of oxidation number higher than those given by Wyckoff<sup>24</sup>. Those unusual oxidation numbers have been studied for octahedral site mostly for oxygenated compounds, for example by Demazeau et al.<sup>25-30</sup>; according to this value  $\delta_m$  and  $\delta_r$  are in good agreement.

Thus, from the study of the monochalcogenides of the 3d metals, we see that each bond which is associated to a large variation in volumes involves one valence electron. Let us now show how this approach can be applied to the case of the phase transformation  $\text{Ce}\gamma \rightleftharpoons \text{Ce}\alpha$ .

### 5. THE PHASE TRANSFORMATION $\text{Ce}\gamma \rightleftharpoons \text{Ce}\alpha$

The difficulty of understanding the properties of cerium is stimulating a great deal of research. One of the problems is to interpret the phase transformation  $\text{Ce}\gamma \rightleftharpoons \text{Ce}\alpha$ . The volume change for this transformation was first attributed to a change of valence from 3 in  $\text{Ce}\gamma$  to 4 in  $\text{Ce}\alpha$  (ref.<sup>1</sup>). From extensive analysis of magnetic susceptibility and metallic radii different intermediate values of the valence<sup>31-33</sup> were proposed.

A possible explanation of the phase transformation can be proposed by comparing the atomic volumes of the different phases of the elements from La to Sm. The atomic volume is that of the cell divided by the number of atoms per cell. The comparison is given in Fig. 4. Table I gives the accurate values with the references. Let us consider

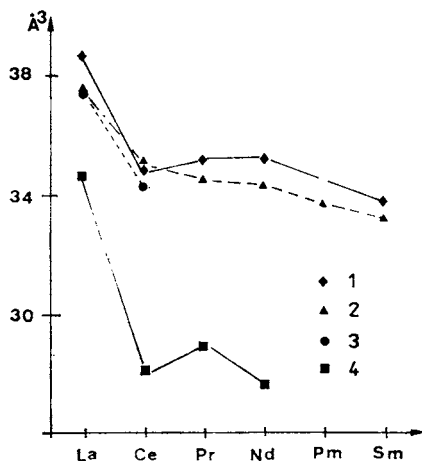


FIG. 4  
Comparison of the atomic volumes of the elements from La to Sm in different phases, 1 b.c.c., 2 d.h.c.p. (double h.c.p.), 3 f.c.c. $\gamma$ , 4 f.c.c. $\alpha$

the relative variation of the atomic volume  $\Delta V/V$  for the same crystal structure between two successive elements. Except between La and Ce they are of the order of one per cent. We consider such value as small variation. We find the same order of magnitude between the  $\beta$ ,  $\gamma$  or  $\delta$  phases of La or Ce. We can understand this as the reflection of different crystal structures, without variation of the number of bonds.

Now let us consider the variation in the atomic volumes when passing from La to Ce, and this for each phase. In each case there occurs a large shrinkage between 7% and 19% according to the phase. We propose to attribute this shrinkage to an additional bond in these different phases of cerium. Now it is easy to attribute this additional bond to the additional electron of cerium in comparison to lanthanum. Thus, already with the body centered cubic phase (b.c.c.), that is the high temperature phase, cerium has these two 6s and the two additional electrons in comparison to barium, implicated each one in a bond.

Therefore, what happens between  $Ce\gamma$  and  $Ce\alpha$ ? Let us consider xenon. This element also crystallizes with the f.c.c. structure as  $Ce\alpha$  and  $Ce\gamma$  but its atomic volume of  $59.5 \cdot 10^6 \text{ pm}^3$  is much larger than that of cerium in whatever the phase<sup>5</sup>. Then, let us consider in cerium the xenon shell. If only the charge of the nucleus was increasing, this should lead to a shrinkage of the xenon shell of the order of 5%. So we must keep in mind that the shape and the size of the xenon shell are modified largely by the bonds of the f.c.c. phase of cerium and the same is true for the other rare earth metals being studied.

Now we must also keep in mind that the xenon gives compounds as for example  $XeF_4$  (refs<sup>40,41</sup>). These two aspects of the phenomena allow to suppose that in  $Ce\alpha$  there is at least one electron of 5s5p shell in the outer most part of the xenon shell,

TABLE I

The atomic volume ( $\cdot 10^6 \text{ pm}^3$ ) of the light rare earths. Between La and Ce we use  $q = (\Delta V(\text{La-Ce})/V(\text{La}))$

Phase <sup>a</sup>	Structure	Rare earth						q
		La	Ce	Pr	Nd	Pm	Sm	
$\delta$	b.c.c.	38.60	35.0	35.22	35.22	—	33.71	0.09
$\gamma$	f.c.c.	37.28	34.37	—	—	—	—	0.08
$\beta$	d.h.c.p.	37.53	34.95	34.56	34.18	33.60	33.04	0.07
$\alpha$	f.c.c.	34.55	28.00	29.05	27.65	—	—	0.19

<sup>a</sup> Atomic volumes are taken from the literature<sup>1,34-39</sup>.

which is involved in a bond giving the reliance  $5r$ . The same hypothesis must hold for the high-pressure phase f.c.c.  $\alpha$  of La, Pr and Nd.

This interpretation is supported by the positron annihilation experiments. According to the hypothesis of a change of valence between  $Cey$  and  $Ce\alpha$  a  $4f$  transfer was expected, one  $4f$  electron or less of  $Cey$  being promoted in the valence band leaving the  $4f$  level of  $Ce\alpha$ . Both, the lifetime of the positrons and the angular correlation of the positron annihilation are sensitive to the valence. So a  $4f$  transfer in the valence band would be seen by the positron annihilation technique. In the case of  $Cey \rightleftharpoons Ce\alpha$  such experiments do not show variation in the number of  $4f$  electrons in the valence band<sup>42-44</sup>.

On the other hand, the isostructural NaCl phase transformation exhibited by SmS or  $Sm_{0.8}Gd_{0.2}S$  is also explained by a transfer of one  $4f$  electron or little less in the valence band. In this case positron annihilation studies exhibit an abrupt drop of the lifetime with the isostructural phase transformation<sup>45,46</sup>. These last results prove that  $4f$  charge transfer can be established by positron annihilation and such a transfer does not exist in the case of  $Cey \rightleftharpoons Ce\alpha$ . So the hypothesis of at least one electron of the  $5s5p$  shell involved in the phase transformation  $Cey \rightleftharpoons Ce\alpha$  is coherent with the conclusion of the positron annihilation experiments. These positron experiments also prove that we can classify SmS in its high-pressure phase<sup>12</sup> with the other, LnS having a small lattice parameter, and that in this case Sm has the reliance  $3r$ .

We think that the exceptional properties of cerium are mainly due to its special position in the periodic table. The  $4f$  electrons involved in a bond are deep, as a result the corresponding bonds are not as strong as similar bond obtained for example with  $3d$  electrons in the case of the  $3d$  elements. So they give a critical value of the atomic volume which allow a further bond with the inner  $5s5p$  shell. This is a different case to those of SmS and TmSe. For SmS we have already shown that its special properties result from its electronic configuration<sup>47,48</sup>. For TmSe, its intermediate value of Curie constant is more a question of bonding than of valency<sup>49</sup>.

## 6. CONCLUSION

In the study of the monochalcogenides of rare earth we found clear evidence of a cation-cation bond. As we have seen, discussing their volume and bonds, this is due to the great homogeneity of their chemical properties. As a result, this fact has led us to presume similar bonds with the monochalcogenides of the  $3d$  metals and to find them. This second step has clearly pointed out the weak role played by the crystal structures, as compared to the number of bonds as a determining factor of the molecular volume. Following the way depicted in third step we have proposed a new interpretation of the phase transformation of  $Cey \rightleftharpoons Ce\alpha$ . In a further work we intend to show that bonds involving inner shell are often present, as well as the classical valence bond.

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