Inorg. Chem. **2008**, *47*, 6475−6481

Inorganic Chemistry
Article

Ahead of the Lanthanide Contraction; Pressure and Ionic Size in the Synthesis of $MSr_2RECu_2O_8$ (RE = Rare Earth, M = Ru, Cr, Ir): a Gaussian Relation[†]

M. Á. Alario-Franco,* R. Ruiz-Bustos, and A. J. Dos Santos-García[‡]

Laboratorio Complutense de Altas Presiones & Laboratorio de Química del Estado Sólido,
Departamento de Química Inorgánica, Facultad de Ciencias Químicas, Universidad Complutense,
28040 Madrid, Spain

Received October 18, 2007

We have been working for sometime on the synthesis at high pressure ($P \leq 12.5$ Gpa) and high temperature ($T \leq 1400$ K) of new materials of the type $MSr_2RECu_2O_8$ (RE = Rare Earth), which formally derive from YBCO (i.e., $CuBa_2YCu_2O_7$) by replacing the [Cu−O_4] squares in the basal plane of the structure by [M−O_6] octahedra (M = Ru, Cr or Ir). The adequate formation of these cuprates, as majority phases, can only be performed in a particular and relatively narrow window of *P* and *T*, outside which they cannot be obtained pure or even obtained at all. These "optimum conditions" bear a remarkable Gaussian correlation with the rare earth ion size, the rare earth cation being at the center of the unit cell in the YBCO setting, and they do not follow the classic lanthanide contraction so often observed in the chemistry of those elements. Instead, *interelectronic repulsion* seems to play a major role in fixing the synthesis conditions. Moreover, the position of the Gaussian tip in the pressure-ionic radii space is also dependent on the transition metal that sits in the octahedron, in a way that seems related to the thermodynamic stability of their simpler oxides.

1. Introduction

In the long search of new materials that followed the discovery of the remarkable HTSC cuprates, a great number of interesting new materials have been found.[1–4] Some of these are the so-called ruthenates or rutheno-cuprates, $RuSr_2RECu_2O_8$ (RE = Rare Earth).[5,6] These materials are remarkable, even if their superconducting T_c is not usually very high in relative terms, because they often show the interesting coexistence of magnetism and superconductivity, two ordered spin states that have usually been reputed as antagonists.[7–9]

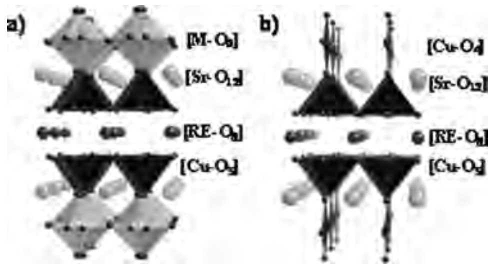

Figure 1. Crystal structures of (a) $MSr_2RECu_2O_8$ with M = Ru, Cr, Ir and (b) YBCO.

As described in detail elsewhere,[10] all these materials are tetragonal and crystallize in space group *P*4/*mmm*, with an average unit cell that is a supercell of the perovskite one and approximate dimensions of $\sim a_p \times a_p \times 3a_p$ (where $a_p \sim 3.9$ Å is the basic perovskite cell parameter). This structure, represented in Figure 1a, is closely related to that of YBCO: $CuBa_2YCu_2O_7$, Figure 1b, if one replaces the copper in the square planar coordination present in the so-called "copper chains", that constitute the charge reservoir layer (CRL)[11,12] for [Ru−O_6] octahedra or, correspondingly,

---

[†] Dedicated to Dimitry Mendeleev in the centenary of his passing away.

* To whom correspondence should be addressed. E-mail: maaf@quim.ucm.es. Fax: +34 91 394 4352.

[‡] Present address: Parque Científico y Tecnológico de Albacete, Instituto de Investìgación en Energías Renovables, Universidad de Castilla-La Mancha, Paseo de la Innovación 1, 02006 Albacete, Spain.

(1) Putilin, S. N.; Antipov, E. V.; Marezio, M. *Physica C* **1993**, *212*, 226.
(2) Schilling, A.; Cantoni, M.; Guo, J. D.; Ott, H. R. *Nature* **1993**, *363*, 56.
(3) Nuñez Regueiro, J.; Tholence, L.; Antipov, E. V.; Caponi, J. J.; Marezio, M. *Science* **1993**, *262*, 97.
(4) Chu, W.; Gao, L.; Chen, F.; Huan, Z. J.; Meng, R. L.; Xue, Y. Y. *Nature* **1993**, *365*, 323.
(5) Bauernfeind, L.; Widder, W.; Braun, H. D. *Physica C* **1995**, *254*, 151.
(6) Ruiz-Bustos, R.; Gallardo-Amores, J. M.; Sáez-Puche, R.; Morán, E.; Alario-Franco, M. A. *Physica C* **2002**, *382*, 395.

10.1021/ic7020676 CCC: $40.75

for chromium or iridium, also in octahedra. The presence of Ru makes the oxygen content equal to eight ions per unit cell, instead of seven as in YBCO or nine as in a triple perovskite $A_3B_3O_9$. In fact, microstructural studies by means of electron diffraction and microscopy have shown[10,13] that the real cell is often tetragonal and sometimes orthorhombic but corresponds, in all cases, to the so-called diagonal cell: $\sim \sqrt{2}a_p \times \sqrt{2}a_p \times 3a_p$.

It is important in what follows to recall that most of the rare earth compounds, and their oxides are no exception, show a remarkable characteristic, which makes many of their properties and in particular their structural dimensions to vary smoothly as a function of Z, that is, as the 4f orbitals are progressively filled. The whole phenomenon is called the *lanthanide contraction*.[14,15] This happens with, for example, the size,[16] polarizability,[17] or melting points[18] of the elements, and also with many properties of their ions and compounds. All these properties decreasing or increasing, periodically, as Z, the atomic number, increases. Yet, the decrease/increase in size with the increase in Z along a period/group is a general trend in all periods/groups of Mendeleev's Periodic Table (Interestingly, only six lanthanide elements were known to Mendeleev: the remaining ones were fit into the periodic table as they were progressively discovered). Nevertheless, there are some nuances to this behavior. For example, the size of the *n*d transition metal atoms or ions show a parabolic relation with Z, the atomic number,[19,20] and not a linear decrease as in the lanthanides or *n*f elements.

Also, an irregular behavior can be observed in some other properties of the lanthanides. This happens, for instance, in their cohesive energies or in the divalent-trivalent valence stabilities of these metals,[21] or indeed in their enthalpies of sublimation (see Figure 4 in reference 22). The most important reason for this irregular behavior is the contribution of the total spin polarization energy, that is, the degree by which the electronic spins of the rare earth ions are aligned in a given direction.

It is worth noting that if the polarization energies are not taken into account, the cohesive energy displays a regular and smooth variation throughout the lanthanide series in accordance with many others properties of the lanthanides.[21]

Back to the M-1212 oxides, it is important to stress that, in their crystal structure, the rare earth ion is eight coordinated by oxygen in the middle of the unit cell—the $^1/_2\ ^1/_2\ ^1/_2$ position in the YBCO unit cell setting. Consequently, along any one of the $MSr_2RECu_2O_8$ families, as Z increases the ionic radii, $^{VIII}r^{3+}_{RE}$, decrease and so do the unit cell parameters. This is in fact the usual trend of the cell parameters in all families of materials that have a rare earth in their structure.[23–25]

We have obtained most of the materials that we are dealing with in here at high pressures and temperatures. Magnetic, electric, thermal, and structural properties have already been published elsewhere.[6,26,27]

In this paper we will concentrate in the problem of the *optimum pressure* (OP) for the synthesis where we have observed a somewhat surprising fact: As will be seen below, the OP, required for their synthesis, does not follow the usual trend of the lanthanide contraction. Instead this pressure shows a remarkable correlation with the RE size, one that can be associated to a Gaussian functionality. We will comment upon these data in this paper and will discuss its possible relation to the interelectronic repulsion within the rare earth cations. It will then be seen that this novel and remarkable behavior shows that size is not the only parameter that controls the synthesis process of these interesting materials.

2. Experimental Section

Of the twenty nine $MSr_2RECu_2O_8$ materials prepared, only three can be made at room pressure (those of Sm, Eu, and Gd with M = Ru) under oxygen at 1323 K according to

$$Sr_2RuREO_6 + 2CuO \rightarrow RuSr_2RECu_2O_8 \qquad (1)$$

However, if one attempts to follow this same procedure for the remaining materials, that is, those requiring high pressure and high temperature, the reaction does not take place: Sr_2RuREO_6 being very unreactive; even at the highest P and T conditions that we can attain (see below) there is no reaction.

This lack of reactivity under pressure of Sr_2RuREO_6 is surely due to the high stability of this double perovskite that, in this context, can be considered a so-called "thermodynamic sink" (Discovering New Oxides: D.A. Vander Griend, S. Malo, T.K. Wang, and K. Poeppelmeier *J. Am. Chem. Soc.* **2000**, *122*, 7308−7311) that prevents other phases to be formed.

Nevertheless, the remaining materials of the $MSr_2RECu_2O_8$ family can be prepared in a two step process.

In the first step, a mixed Sr−Cu oxide of adequate stoichiometry was prepared by heating in air, for 2 days at 1323 K, $SrCO_3$ and CuO as reagents according to the following reaction:

---

(7) Ginzburg, V. L. *Zh. Exsp. Teor. Fiz.* **1956**, *31*, 202.
(8) Bernd, L.; Ching-Wu, C. *Nat. Mat.* **2005**, *4* (7), 516.
(9) Fauré, M.; Buzdin, A. I. *Phys. Verh. Lett.* **2005**, *94*, 187202.
(10) Mclaughlin, A. C.; Zhou, W.; Attfield, J. P.; Fitch, A. N.; Tallon, J. L. *Phys. Rev. B.* **1999**, *60*, 7512.
(11) Tokura, Y.; Takagi, H.; Uchida, S. *Nature* **1989**, *337*, 345.
(12) Alario-Franco, M. A. *Adv. Mater.* **1994**, *7* (2), 229.
(13) Aguirre, M. H.; Ruiz-Bustos, R.; Alario-Franco, M. A. *J. Mater. Chem.* **2003**, *13* (5), 1156.
(14) Huheey, J. E.; Keiter, E. A.; Keiter, R. L. *Inorganic Chemistry*, 4a ed.; Harper Collins College Publishers: New York, 1993; p 603.
(15) Greenwood, N. N.; Earnshaw, A. *Chemistry of the elements*, 1st ed.; Pergamon Press: Elmsford, NY, 1984; p 1431.
(16) Shannon, R. D.; Prewitt, C. T. *Acta Crystallogr.* **1976**, *A32*, 751.
(17) Grimes, N. W.; Grimes, R. W. *J. Phys.: Condens. Matter.* **1998**, *10*, 3029.
(18) *CRC Handbook of Chemistry and Physics*, 73rd ed.; Lide, D. R., Ed.; CRC Press, Inc.: Boca Raton, FL, 1992; pp 4−122.
(19) Bell, J. A. and the American Chemical Society. *Chemistry. A project of the American Chemical Society*; W. H. Freeman: New York, 2004.
(20) Atkins, P. W. *Physical Chemistry*, 4a ed.; Oxford University Press: New York, 1990.
(21) Melsen, J.; Wills, J. M.; Johansson, B.; Eriksson, O. *J. Alloys Compd.* **1994**, *209*, 15.
(22) Nugent, L. J.; Burnett, J. L.; Morss, L. R. *J. Chem. Thermodyn.* **1973**, *5*, 665.
(23) Mitchell, R. H. *Perovskites: Modern and Ancient*; Almaz Press: Ontario, Canada, 2002.
(24) Marezio, M.; Remeika, J. P.; Dernier, P. D. *Acta Crystallogr. B* **1970**, *26*, 300.
(25) Marezio, M.; Remeika, J. P.; Dernier, P. D. *Acta Crystallogr. B* **1970**, *26*, 2008.
(26) Ruiz-Bustos, R.; Aguirre, M. H.; Alario-Franco, M. A. *Inorg. Chem.* **2005**, *44*, 3063.
(27) Dos santos-García, A. J.; Aguirre, M. H.; Morán, E.; Saéz-Puche, R.; Alario-Franco, M A. *JSSC* **2006**, *179*, 1275.

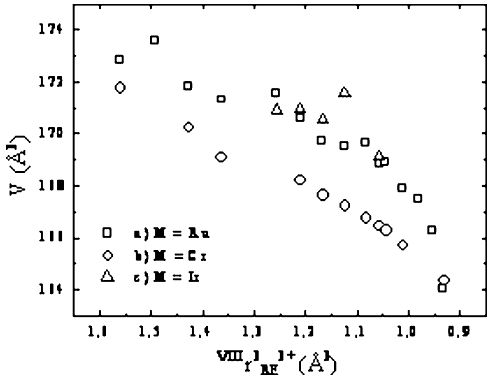

Figure 2. Variation of the unit cell volume for each of the three families as a function of the cube of oxygen eight-coordinated rare earth ionic radii.[16]

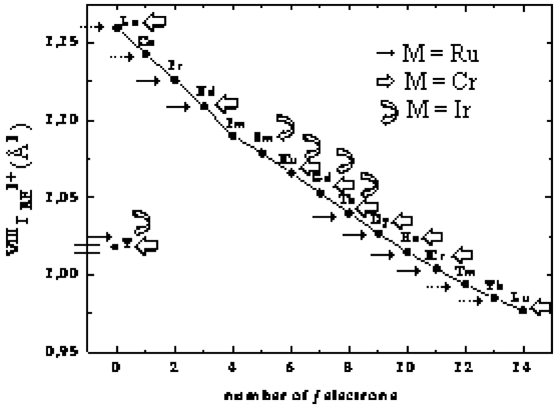

Figure 3. Representation of the lanthanide contraction as the octacoordinated ion radius versus the number of f electrons. Overimposed on it, different arrows are used to indicate the members of the $MSr_2RECu_2O_8$ families obtained. Dashed arrows are used for phases where less than 50% of pure phase was obtained while the gray ones show the three ruthenium compounds prepared at room pressure.

$$SrCO_3 + CuO \rightarrow SrCuO_2 + CO_2 \qquad (2)$$

In a second step, this precursor was mixed with the corresponding RE_2O_3 rare earth oxide, where RE = Y, La−Lu (except for Tb and Pr where Tb_4O_7 and Pr_6O_{11} were used) and the corresponding transition metal dioxides. After thoroughly grounding the previous oxides, these were placed in a crucible and treated at high pressure and temperature according to

$$2SrCuO_2 + \frac{1}{2}RE_2O_3 + MO_2 + \frac{1}{4}O_2 \rightarrow MSr_2RECu_2O_8 \qquad (M = Ru, Cr, Ir) \quad (3)$$

The majority of the experiments, that is, those leading to the complete Ru-1212[6] and Cr-1212[26] series and many of the Ir-1212 phases,[27] were performed in a Belt type apparatus located in the Laboratorio Complutense de Altas Presiones of the Universidad Complutense de Madrid.[28] This press allows one to work simultaneously at pressures up to 80 Kbar and temperatures close to 1673 K. Gold and platinum capsules were used as crucibles at moderate and higher temperatures, respectively.

On the other hand, for the materials requiring pressures higher that 80 Kbar, namely, the irido-cuprates of Tb,[29,30] Y, and Nd, a Walker-type multianvil pressure module located at the Ludwig-Maximilians- Universität München[31] was used. This allows to reach pressures up to 150 Kbar and temperatures of 1673 K.

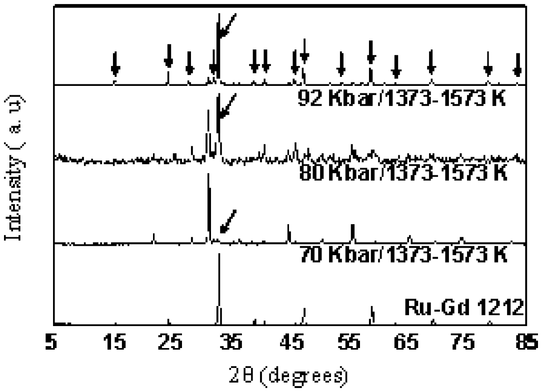

Figure 4. X-ray patterns for three $IrSr_2TbCu_2O_8$ samples synthesised at different pressures. Reflections corresponding to the 1212 phase are marked with black arrows. The $RuSr_2GdCu_2O_8$ X-ray pattern is displayed as a visual reference.

Samples were characterized by X-ray powder diffraction (XRPD), and these patterns were refined with the Rietveld procedure using the GSAS[32] and Fullprof_Suite packages.[33] Unit cell volumes are plotted in Figure 2. It can be seen that they decrease as the lanthanide radii decrease.

Sample compositions were checked by EDS (Link Pentafet 5947 Model, Oxford Microanalysis Group) in a Jeol JEM FX200 transmission electron microscope (TEM) by in situ observations. High resolution electron microscopy images (HREM) and selected area electron diffraction diagrams (SAED) were performed on a Jeol JEM 3000FX and 4000FX microscopes.

3. Results

Twenty nine different materials, of general formula $MSr_2RECu_2O_8$, have been prepared. These are schematically indicated by arrows in Figure 3 overimposed in a graphic of the lanthanide contraction. In this one, the radii of the trivalent lanthanide cations[16] in 8-fold coordination $^{VIII}r^{3+}$, which is the coordination of the rare earth ion in the M-1212 structure, are plotted versus the number of f electrons that they have. This well-known decreasing trend is due to the characteristics of the f orbitals and has a great influence in the chemistry of these elements.[14,15,34] A full/broken arrow in Figure 3 signifies that the expected cuprate has been obtained in a bigger/smaller amount than 50% of the reaction products in the respective synthesis processes. To obtain still bigger amounts of the concerned cuprate products will be both rather expensive and time-consuming and will not really add much information to the discussion that follows. It is worth mentioning that, as seen in Figure 3, the lanthanide contraction shows a discontinuity halfway between f^0 La(III) and f^{14} Lu(III), corresponding to the (very stable) f^7 Gd(III), configuration.

---

(28) http://www.ucm.es/info/labcoap/.

(29) Dos santos-García, A. J.; van Duijn, J.; Saez-Puche, R.; Heymann, G.; Hupertz, H.; Alario-Franco, M. Á. *JSSC* **2008,** *181*, 1167.

(30) Dos santos-García A. J. *Ph.D. Thesis*, Universidad Complutense de Madrid, Spain, 2007.

(31) http://www.cup.uni-muenchen.de/ac/hupertz/.

(32) Larson, A. C.; von-Dreele, R. B. *General Structure Analysis System (GSAS)*; Report LAUR 86−748; Los Alamos National Laboratories, Los Alamos, NM, 1990.

(33) Rodríguez-Carvajal, J. *Phys. B* **1993**, *192*, 55.

(34) Cotton, F. A.; Wilkinson, G.; Gaus, P. L. *Basic Inorganic Chemistry*; Wiley: New York, 1995; p 600.

(35) Ruiz-Bustos, R.; Dos santos-García, A. J.; Alario-Franco, M. A. *Z.A.A.C.* **2008**, *633*, 1919.

The case of the Tb(III) irido-cuprate is very illustrative of the whole phenomenon we are going to discuss.[29] Figure 4 shows the powder X-ray diffraction patterns for $IrSr_2TbCu_2O_8$ obtained at different pressures and the same temperature and time. The patterns can be indexed on the tetragonal cell characteristic of this family of compounds; it is clearly seen that, as the pressure is increased, the percentage of 1212 phase does also increase. It can also be observed that at 92 Kbar the material is practically pure.[29] A similar plot concerning the case of $RuSr_2PrCu_2O_8$ was given on reference 35.

We can now establish the concept of OP as the pressure range at which the material can be obtained. What this means is that for pressures below OP, the synthesis reaction does not take place, that is, the activated complex is not attained. On the other hand, at pressures above OP a different reaction takes place and the M-1212 cuprate cannot be made. At pressures below OP, one does not obtain the phase, while at pressures higher than OP either it does not form or it decomposes, usually according to the reaction

$$MSr_2RECu_2O_8 \rightarrow Sr_2REMO_6 + 2CuO \qquad (4)$$

which is the reverse of reaction 1 and originates the interesting Sr_2RECuO_6 double perovskites.[36–38]

As a matter of fact, OP is not really a single, precisely determined pressure but, as is common in all chemical reactions, the reaction takes place, although at different rates, in a certain pressure range at a given temperature or vice versa. It is also important to point out that, in high pressure synthesis, impurities are commonly observed. This is particularly true in the present case where we have four different metallic elements three of which can have different oxidation states. The potential number of impurities is indeed substantial. We have relied on XRPD for the detection of the obtained material, so that the above indicated margin refers to conditions under which the expected M-1212 cuprate is detected by these means; but we have in all cases confirmed this point by using SAED and HREM as well as EDX *in situ* in the electron microscope.

Figure 5 shows, as a function of $^{VIII}r^{3+}_{RE}$, the value of the OP required for the synthesis at 1373−1573 K, of the different members of the three families of cuprates $MSr_2RECu_2O_8$ that we have, so far prepared, with, respectively, M = Ru, Cr, or Ir in the CRL.

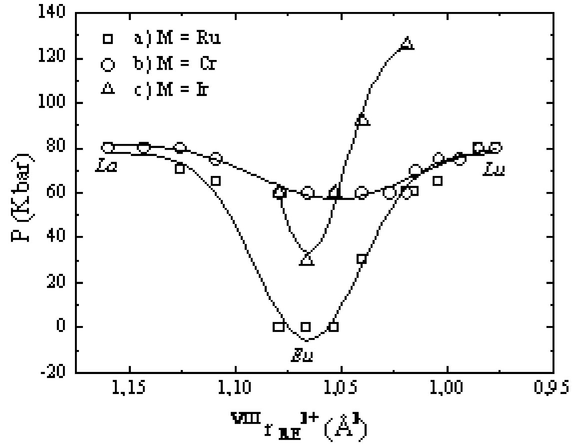

Figure 5. OP required for the synthesis of the $MSr_2RECu_2O_8$ families versus the rare earth ionic radii.[16]

It is clear from Figure 5 that OP changes markedly with $^{VIII}r^{3+}_{RE}$. In the case of the rutheno-cuprates family (Figure 5a), the first part of the plot, that is, from the bigger La^{3+} ($^{VIII}r^{3+}_{La}$ = 1.16 Å, OP ~ 80 Kbar) to the middle sized rare earth, Sm^{3+}, ($^{VIII}r^{3+}_{Sm}$ = 1.08 Å, OP ~ 1 atm), OP markedly decreases, so that the smaller the rare earth is the smaller is the pressure required for its synthesis. This is in a good correlation with the lanthanide contraction. Following this trend, then, the Sm^{3+} compound can actually be made at room pressure. This kind of behavior, commonly described as a size effect, is often taken as an indication of the preeminence of ionic bonding in the corresponding family of lanthanide based solids.[24,25] Once the middle of the series has been attained, OP remains constant and both the Eu^{3+} and Gd^{3+} isomorphous rutheno-cuprates can also be prepared at room pressure.[5] In fact, the relative simplicity of the preparation of this last material, $RuSr_2GdCu_2O_8$, at room pressure, together with its interesting electronic and magnetic properties, have led to much recent work to study its transport and other properties.[39–41]

Yet, the following rare earths (i.e., from Tb^{3+} to Lu^{3+}) require an OP that increases with decreasing size (OP for Tb^{3+} is ~ 30 Kbar; for Er^{3+} it is ~ 60 Kbar and ~80 Kbar for Yb^{3+} and Lu^{3+}, Figure 5). This is in clear opposition with the previous trend and, indeed, out of the usual parallelism with the lanthanide contraction. In fact, as clearly seen in Figure 5, a Gaussian relation seems to exist between the size of the rare earth ion present in the cuprate and the OP required for its synthesis.[30,35,41] In other words, in the well-known M-1212 structure, Figure 1a, the size of the RE cation, which occupies the unit cell center, controls the synthesis conditions, a really not unexpected fact: Many properties, including the synthesis of many different compounds, whether with rare earths or not, do depend on the ionic size. What is unusual is the fact that the relation observed in here follows a Gaussian trend and that, all other synthesis conditions being equal, in particular for a certain temperature, a higher pressure is needed to make the materials both with the smaller and the bigger cations than with the intermediate ones.

Figure 5b is a similar plot for the family of chromo-cuprates: $CrSr_2RECu_2O_8$. Again, a Gaussian trend is observed, but there are a couple of interesting nuances which are worth mentioning. First of all, the minimum OP to prepare any of the chromo-cuprates is always well over room pressure: OP ≥ 60 Kbar. This certainly reflects

---

(36) Doi, Y.; Hinatsu, Y. *J. Phys.: Condens. Matter* **1999**, *11*, 4813.

(37) Battle, P. D.; Goodenough, J. B.; Price, R. *J. Solid State Chem.* **1983**, *46*, 234.

(38) Saéz-Puche, R.; Climent-Pascual, E.; Ruiz-Bustos, R.; Alario-Franco, M. A.; Fernández-Díaz, M. T. *Prog. Solid State Chem.* **2007**, *35* (2−4), 211.

(39) Mclaughlin, A. C.; Attfield, J. P. *Phys. Rev. B* **1999**, *60*, 14605.

(40) Klamut, P. W.; Dabrowski, B.; Kolesnik, S.; Maxwell, M.; Mais, J. *Phys. Rev. B* **2001**, *63*, 224512.

(41) Ruiz-Bustos, R. *Ph.D. European Thesis*, Universidad Complutense de Madrid, Madrid, Spain, 2003.

Table 1. Parameters Obtained after Fitting the Plots in Figure 5 to a Gaussian Distribution Curve

M-1212	Ru	Cr	Ir
central radius (r_c)	1.066(1)Å	1.053(7) Å	1.066(1) Å
dispersion (σ)	0.05007	0.07235	0.04974

the instability of Cr(IV) oxides. CrO_2 itself is a metastable high pressure phase[42,43] that decomposes, at room pressure, at a rather low temperature for a transition metal oxide: 623 K in air and somewhat higher, ~ 673 K, in oxygen at 1 atm.[44] Also, the number of chromo-cuprates that can be prepared at this threshold OP is higher than in the ruthenium case: the chromocuprates of the trivalent Y, Dy, Tb, Gd, Eu, and Sm can all be made at ~ 60 Kbar. This is undoubtedly related to the previous point because all of these cations did form the rutheno-cuprates at or below such an OP. The chromo-cuprates of Nd^{3+} and Ho^{3+} can be formed at ~70 Kbar and the Er^{3+} one at ~ 75 Kbar. In contrast, the $CrSr_2RECu_2O_8$ compounds corresponding to bigger Pr^{3+} and La^{3+} and smaller Yb^{3+} and Lu^{3+} ions require the maximum pressure for this family: ~80 Kbar, Figure 5b. Ion size and OP are also intimately related in the chromo-cuprates and, again, with a Gaussian relation even if, in this case, the curve is rather flattened because of, as mentioned above, the metastability of CrO_2. Once the conditions to stabilize Cr (IV), the Gaussian minimum and ~60 Kbar at this temperature, are met, the situation is rather similar to the ruthenium case.

The iridium case, shown in Figure 5c is somewhat intermediate between those of ruthenium and chromium: The threshold OP to obtain the irido-cuprates is ~30 Kbar, which corresponds to $IrSr_2EuCu_2O_8$. Here there are also some interesting points to be mentioned: for both the Gd^{3+} and Sm^{3+} compounds OP is ~60 Kbar while for the small cations, $Tb^{3+}$and Y^{3+}, OP is much higher: 92 and 126 Kbar, respectively. It is to be remarked that, although the compounds containing the smaller RE cations are actually made at much higher pressures, the Gaussian trend is also present as one can see in Figure 5c.

We have been able to fit the data shown in Figure 5 to a Gaussian function:

$$P(r) = \frac{1}{\sigma\sqrt{2\pi}} e^{-2\left(\frac{r - r_c}{\sigma}\right)^2} \tag{5}$$

where $P(r)$ is the OP, r is the Shannon and Prewitt[16] rare earth radius, and r_c the value of r at the Gaussian minimum. Table 1 shows the r_c values and the dispersion corresponding to the three plots.

We have not yet prepared the iridates corresponding to the bigger cations; they require pressures over 80 Kbar. However, in the Nd case, samples prepared at increasing pressures show a trend similar to the Tb case shown in Figure 4: The higher the pressure the greater the amount of the $IrSr_2NdCu_2O_8$ material. One can then predict that if, as obviously expected, the Nd(III) case follows the corresponding Gaussian trend, it could be prepared pure or almost pure at ~120 Kbar.

4. Discussion

This common trend, shown for the three different M-1212 family of compounds that we have prepared, is quite different from what one could expect from the lanthanide contraction. It is interesting to recall that this contraction concerns both the RE elements and many of the properties of the compounds in which they are involved. Yet, there are cases in which this behavior is not sustained. Among them, one of the earlier one appears to be the partition of the lanthanide RE(III) ions in their liquid−liquid extraction data in different solvents (refs 45, 46, and references therein).

It was observed in those experiments that, instead of a simple decrease of the equilibrium constant (which corresponds to the ratio of the concentration of the metal cation in the organic phase to that in the aqueous one) paralleling to the size of the rare earth, a more elaborated plot is obtained. This consists of a kind of a slightly increasing sinusoidal plot, (Figure 1 in ref 46) in which, in addition to the expected discontinuity at the 1/2 point corresponding to the f^{7} configuration, attributed to the half-filled shell stabilization effect in the electronic structure of Gd(III), there were two minor dips: one at the 1/4 point, between elements 60 and 61, and another one at the 3/4 point, between elements 67 and 68.

This led Peppard et al. to establish a so-called “tetrad effect”, according to which, “in systems involving the 15 lanthanides, including Y, the logarithm of a suitable numerical measure of a given property versus Z, may be grouped by four tetrads with Gd being in the middle (see Figure 13 in ref 45).

Nugent et al. explained the tetrad effect following a model by Jorgensen of the nephelauxetic effect[47] based in the interelectronic repulsions taking place in the f orbitals that, obviously, change substantially with the number of electrons that occupy them as Z varies. The corresponding results of this work are collected in Figure 2 of ref 46, where the main contributions to the stabilization energy $H_{s\text{-}r}$, are plotted as a function of q. It is seen there that the main contribution, the spin pairing energy, is responsible for the 1/2 dip at the half-filled configuration; this corresponds to a stabilization of the Gd(III) configuration of ~ 10 Kcal/mol. On the other hand, the orbital polarization, which is about 6 times smaller in magnitude appears to control the tetrad effect and is responsible for the dips observed at 1/4 and 3/4 occupation configurations.[46] This last is in fact somewhat helped by the third term, the spin−orbit coupling stabilization energy, which is, however, quite smaller, about half the orbital polarization contribution.

---

(42) Kubota, B. *J. Am. Ceram. Soc.* **1961**, *44*, 239.
(43) White, W. B.; Roy, R. *Geochim. Cosmochim. Acta* **1975**, *39*, 803.
(44) Alario-Franco, M. A.; Sing, K. S. W. *J. Therm. Anal.* **1972**, *4*, 47.
(45) Peppard, D. F.; Bloomquist, C. A.; Horwitz, E. P.; Lewey, S.; Mason, G. W. *J. Inorg. Nucl. Chem.* **1970**, *32*, 339.
(46) Nugent, L. J. *J. Inorg. Nucl. Chem.* **1970**, *32*, 3485.
(47) Jorgensen, C. K. *J. Inorg. Nucl. Chem.* **1970**, *32*, 3127.

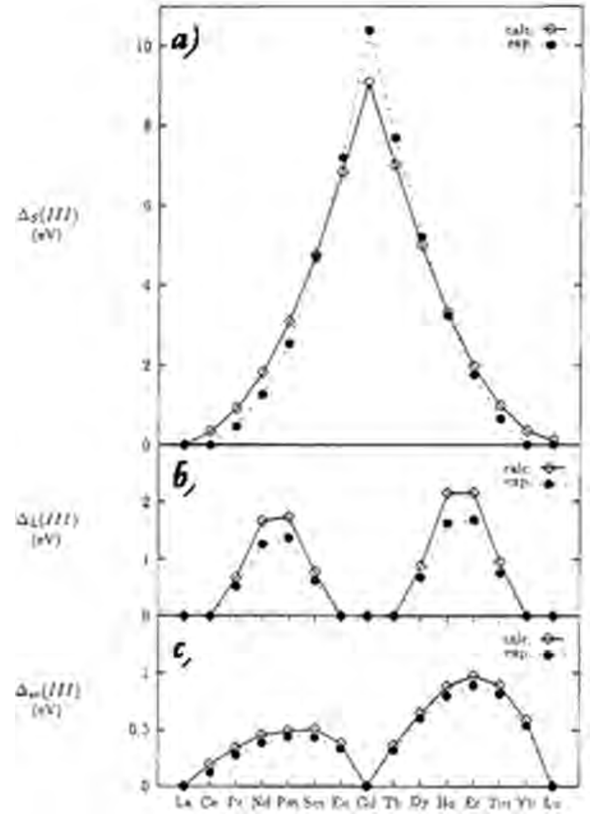

Figure 6. Calculated (empty circles) and experimental values (filled circles) of the contributions to the polarization energy of the 3+ oxidation state of the lanthanides. From top to bottom: spin polarization energy, orbital polarization energy, and spin−orbit coupling energy (reproduced with permission from ref 21).

Somewhat more recently, the influence of the polarization energy in the lanthanide properties has been tackled by Melsen in some calculations[21] and the results of this work, although somewhat less precise than the experiments, give a similar pattern and corroborate the essential part of the earlier Nugent plot.[46] The spin polarization was calculated by means of the Local Spin Density Approximation. The calculation of the intrashell electronic energy involves obviously the three terms used by Nugent et al. referred to above: The spin polarization (pairing) energy Δ_s (related to the E^1 Racah parameter,[20] the orbital polarization energy, Δ_L (related to the E^3 Racah parameter), and the spin−orbit interaction energy, $\Delta_{s\text{-}o}$ associated to a spin−orbit coupling parameter ξ. These three parts correspond to Hund's first, second, and third rules, respectively. Details can be obtained in ref 21. The calculations, Figure 6, then confirm that the largest contribution to the total polarization energy comes from the spin-pairing energy. This one is quite large for the middle elements of the series because of the number of f electrons that favor a maximum spin. On the other hand, orbital polarization, Figure 6b, and spin−orbit coupling, Figure 6c, energies are much smaller than the spin polarization energy (Figure 6a). The first one is actually zero in the central lanthanide ions. Yet, as observed above and already remarked by Nugent et al., this small contribution seems to be responsible for the intermediate dips at 1/4 and 3/4 observed in the tetrad effect.[46]

It can be seen in Figure 6 that both the experimental and the calculated data for $H_{s\text{-}p}$ essentially reproduce the shape of the *inverse* of our OP versus rare earth size Gaussian relation of Figure 5. Or, expressed in words: the more stable configurations of the f^q trivalent lanthanides are, due to their greater spin pairing energy, those at the middle of the series, and this is what is observed in Figure 5. It then appears that the easiness of preparation of the M-1212 materials is closely related to the stability of the Ln(III) ions in terms of the interelectronic spin pairing energy. A most interesting result!

This kind of relation can be translated into thermodynamic data, as done by Nugent[22] and Table 1 of that reference collects the corresponding values for $\Delta H^0_{\{\mathrm{M(III)}\}}$, the standard formation enthalpy of the hydrated Ln(III) ions. When these data were plotted as a function of Z (Figure 2 of ref 22) they show a similar functionality, as our own, with a difference in energy between $\Delta H^0_{\{\mathrm{La(III)}\}} \approx \Delta H^0_{\{\mathrm{Lu(III)}\}} \sim$ 168.8 Kcal/mol and $\Delta H^0_{\{\mathrm{Gd(III)}\}} \sim$ 163.0 Kcal/mol of the order of ~3.5%. Although it is obvious that there are clear experimental differences between a hydration process and a high temperature reaction such as the synthesis of the M-1212 cuprates, we should notice that both of them follow an analogous trend with respect to the lanthanide size or, equivalently, with respect to q or to Z. This is nevertheless logical and rooted in the basis of Chemistry as described in the "Activated Complex Theory" and the subsequent developments.[20,48] So far we have used what one can call the "chemical approach" to the influence of the interelectronic repulsion stabilization energy to the problem.

An equivalent one is to consider it in terms of the Mott-Hubbard model for condensed phases where, considering the many-body problems confronted in dealing with the all electron repulsion in solids, one only takes into account intra-atomic repulsion effects, that is, between two electrons on the same atoms. From there on, see, for example, Cox in reference 49, one defines a Hubbard parameter U which can be assimilated to the difference between the corresponding ionization potential and electron affinities for the atom in question. In particular, in the lanthanide case, one deals with the energy corresponding to the process:

$$2(4f)^n \rightarrow (4f)^{n+1} + (4f)^{n-1} \tag{6}$$

The respective U values for the lanthanide metals and some of its compounds have been obtained from Photoelectron Spectroscopy (PES) and they are, as expected, in fair agreement with those shown above from experimental and calculated data from Melsen[21] and Nugent,[46] respectively. In fact, when the Hubbard values for the La to Lu elements are represented versus z, as in Figure 5.4 of ref 49, one observes a plot similar to the tetrad effect, something that has been unnoticed until now, and indeed, similar to our Gaussian relation. This is a kind of satisfying self-consistency.

---

(48) Eyring, H. *J. Chem. Phys.* **1935**, *3*, 107.

(49) Cox P. A. *The Electronic Structure and Chemistry of Solids*; Oxford University Press: New York, 1987; p 140.

5. Conclusions

We have shown in here that the optimum synthesis conditions for the 29 compounds corresponding to three families of M-1212 cuprate that we have prepared, with the help of high pressure at high temperature, show a Gaussian functionality with the rare earth characteristics—size, Z, number of f electrons—that can be attributed to differences in stability of the f^q electron configuration due to interelectronic repulsions. This also means that an apparently irregular behavior, such as the deviation from the lanthanide contraction, is not that irregular.

The dip observed mid way for the OP as a function of Z, that is, the Gaussian minimum, appears to be related to the relative stability of the corresponding oxidation state of the M transition metal cations that occupy the octahedral positions.

This is, to our knowledge, the first example of the influence of the intra-atomic interelectronic repulsions in the course of a synthesis reaction, without affecting the structural properties of the resulting products which, by themselves, effectively comply to the lanthanide contraction as seen in Figure 3. This by itself seems to indicate that the intra-atomic interelectronic repulsions essentially affect the kinetic and not the thermodynamic basis of the synthesis reaction: a remarkable result worthy of further investigation.

Comments on the Nature of Scientific Inquiry. Before closing, a couple of recent articles are worth comment in the light of the above findings. The first one, by Seifert,[50] concerns the melting points of the lanthanide trichlorides, "an unsolved problem" according to its author. It is seen there that this property of the $RECl_3$ phases decreases from $LaCl_3$ to $TbCl_3$ by 24.0% and then increases by 27.2% to $LuCl_3$: a huge amount, indeed! A similar trend is also observed for the melting enthalpies. Because the lattice energies of these materials do follow the trend expected for the lanthanide contraction, that is, "they increase continuously with decreasing the trivalent radii, from the La to the Lu compounds",[50] those interesting phenomena are tentatively "attributed to the structural features of the liquid" and we are warned that more quantitative work is necessary. Notwithstanding that the melting point of a substance is indeed dependent on both the solid and the liquid, in the light of the observed importance of the intra-atomic interelectronic repulsion of the f^n configurations in the above-reported properties, it will be interesting to look for an alternative or, at least, complementary explanation along the lines developed in this paper concerning interelectronic repulsions for the clear explanation of the thrichloride properties.

The second, more recent article, by Evans,[51] concerns "The importance of questioning scientific assumptions: Some lessons from f element chemistry". In this most interesting article, after quoting Faraday, and Cajal and Smalley, both of them of Nobel Prize fame, for teaching us "to be in doubt of anything which it is not obvious", it beautifully uses the lanthanide contraction so as to perform "the synthesis of unconventional long bond organometallics overturning the rules in the area" and makes a lot of new chemistry by pushing the barriers of conventional assumptions.

The above results concerning the synthesis reactions of those M-1212 cuprates are certainly on the same line: questioning the *universality* of the value of the very lanthanide contraction. Yet, we could find a plausible explanation of our results by looking back to previous workers in the field of lanthanide chemistry.

Obviously, Newton's remark that we are "dwarfs in the shoulders of giants" is as valid as ever, and Mendeleev was certainly one of those giants.

Acknowledgment. We thank P. Dozent, H. Hupertz and G. Heymann for making the Tb and Y irido-cuprate samples and Prof. E. Morán and Prof. R. Sáez-Puche for valuable comments. Financial support from Ministerio de Educación y Ciencia (MAT 2004-01641 and the Juan de la Cierva program), Comunidad Autonóma de Madrid (S-505/PPQ/0358-Project MATERYENER), and the Areces Foundation is also gratefully acknowledged.

IC7020676

---

(50) Seifert, H. J. *J. Therm. Anal. Calorim.* **2005**, *82*, 575.

(51) Evans, W. J. *Inorg. Chem.* **2007**, *49* (9), 3435.