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The Cation Arrays in the Garnet-Type $Al_5Ln_3O_{12}$ and Perovskite-Like $AlLnO_3$ Compounds

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The crystal structures of garnet-type $Al_5Ln_3O_{12}$ and perovskite-like $AlLnO_3$ compounds are analyzed on the basis of the cationic array. In both structural types a clear relationship can be established between the lanthanide subarrays in the oxides and their parent metallic bcc phase. In contrast, the aluminum subarrays show no similarity to metallic aluminum. In the perovskite-like $AlLnO_3$ compounds there is also a direct correspondence, in distances and topology, with CsCl-type alloys of formula Al*Ln*. © 1997 Academic Press

INTRODUCTION

In previous papers we have reported several examples of compounds in which cation arrays can be seen as fragments or deformations of the parent metal structure resulting from the inclusion of other atoms or atomic groups (1–4). This new approach can be considered an extension of the new model reported by O'Keeffe and Hyde (5), which described the structures of oxides as oxygen-stuffed alloys as an alternative to the traditional model of cation-centered anion polyhedra.

As a part of a systematic study of Al-containing compounds, we have reported the relationship between the Al subarray in oxides, hydroxides, and oxyhydroxides and the structure of fcc Al (6, 7). As a continuation of this work, we report here an analysis of the cation arrays in two families of Al-containing compounds: the garnet-type $Ln_3Al_5O_{12}$ compounds and the perovskite-like $AlLnO_3$ compounds. It should be noted that in both cases the Al subarray cannot be related to the structure of fcc Al. Instead, the structures seem to be governed by the lanthanide subarrays, which show a clear relationship to the structures of elemental bcc *Ln*.

DISCUSSION

The garnet structure, typified by grossularite, $Ca_3Al_2Si_3O_{12}$, is the structure type of the $(Ln)_3M(1)_2M(2)_3O_{12}$ compounds (M = Fe, Al, Ga; Ln = lanthanide). It is cubic, space group $Ia\bar{3}d$, $Z = 8$. It has been described as a 3D network of AlO_6 octahedra which share their six vertices with six SiO_4 tetrahedra. The large cations (Ca) occupy the interstices of this network and are coordinated by eight oxygens forming a distorted polyhedron which is between a cube and a dodecahedron.

Hyde and Andersson (8) have described the structure in terms of a bcc rod packing, each rod consisting of alternating octahedra and empty trigonal prims sharing faces along the nonintersecting trigonal axes of the cell. Cations $M(1)$, in special position 16a (0, 0, 0), are at the centers of these O_6 octahedra. Between these polyhedral rods, there are tetrahedral interstices occupied by $M(2)$, which are in the special position 24d (3/8, 0, 1/4), and twisted cubes occupied by *Ln* atoms, in the special position 24c (1/8, 0, 1/4).

O'Keeffe and Hyde (5) refer to an old description of the structure attributed to Geller (9), which is based on their cation subnet. It forms an array of the Cr_3Si type in which each O atom is coordinated by two Ca atoms, one Al atom, and one Si atom, forming a distorted tetrahedron. We must add, however, that in the given reference (9) we have not found such a description of the structure. The Gd_3Al_5 array is represented in Fig. 1. It is defined by the following M–M distances: Gd–Gd, 3.709×4; Al(1)–Gd, 3.386×6; Al(2)–Gd, 3.028×2 and 3.709×4; Al(1)–Al(2), 3.386×6; and Al(2)–Al(2), 3.709×4 Å. As seen, the Al–Al distances are greater than those in elemental Al (2.86 Å) in such a way that, even with Al being the majority element, no relationship can be established with its fcc structure. The *Ln*–Al distances are of the order of distances found in real *Ln*–Al alloys. Thus, the value of 3.028 Å in $Al_5Ho_3O_{12}$ is similar to the value of 3.004 Å occurring in the Cu_3Au-type Al_3Ho and that of 3.354 Å in $Al_5Tb_3O_{12}$ is comparable to the value of 3.389 Å for the Tb–Al distance in Tb_3Al, also of the Cu_3Au type. The coincidence is not only in distances but also in

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topology. In fact, the Al atoms which center the cubes of Fig. 1 and the Ln_3 triangles, shaded in the figure, are part of the Al-centering Ln_{12} cubooctahedra existing in the AlLn_3 alloys (see Fig. 2). In the same way the –*Ln*–Al–*Ln*– rows centering the faces of the cubes in Fig. 1 are equal to the same rows existing in the Al_3Ln alloys. Thus, parts of the structures of the alloys in the *Ln*–Al system can be recognized in the garnets.

The *Ln*–*Ln* distances are of the order of those found in the elements. The *Ln* array is represented in Fig. 3. It is formed by two identical 3D nets of equilateral triangles sharing corners to form condensed cycles of 10 triangles. These nets can be thought as derived from the bcc phase of the parent metal. A bcc net can be decomposed into two similar interpenetrated subnets, as seen in Fig. 4. Opening this array, separating the two subnets, and rotating the triangles around the common atom would give rise to the array observed in the garnet. This opening of the structure is made in such a way that the shortest contacts between atoms of the two subnets are comparable to the distances of the third neighbors in the bcc net and the contacts between atoms of the same subnet correspond to the distances of the fourth nearest neighbors in the element. These contacts are indicated by *ab* and *aa* in Fig. 3 and the values are collected in Table 1. It should be pointed out that in the bcc metals the triangles are not equilateral but are formed by an edge of the unit cell and the atom centering the cell. These three distances should be regularized, giving a mean value that is equivalent to the distances observed in the garnets. Both sets of distances are collected in Table 1 and as can be seen, the deviations are of the order of 2–3% except for the anomalous Eu and Yb, whose metal phases show distances 7–10% longer than those in the garnet-type oxides. In the other lanthanide garnet-type compounds, $Ln_3M_5O_{12}$ (M = Fe, Ga), the deviations of the *Ln*–*Ln* distances from those observed in the elements are of the order of 6%. A similar mechanism has been proposed for the formation of the C–Ln_2O_3 compounds, based on the decomposition of

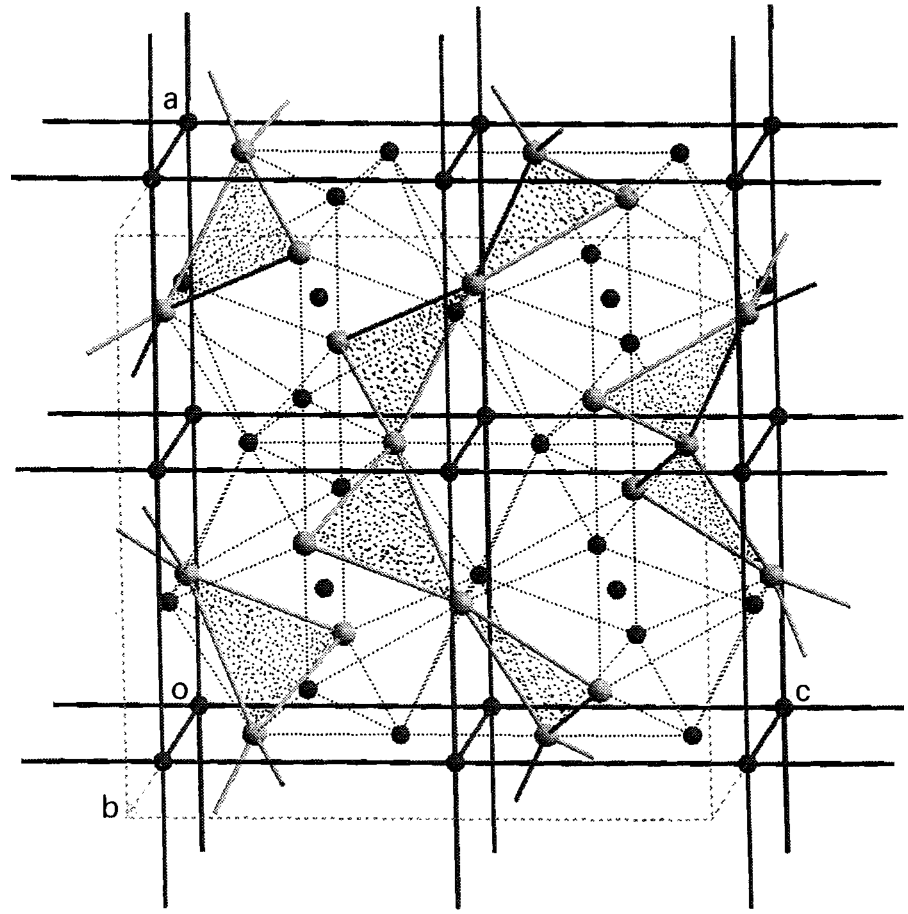

FIG. 1. Perspective view of half of a unit cell (four cubes) of a $Ln_3Al_5O_{12}$ garnet showing the cation array, which adopts the structure of the Cr_3Si type. Gray circles represent *Ln* atoms and black circles represent Al atoms. Solid lines connect the *Ln* atoms forming corner-sharing Ln_3 triangles. Dotted lines connect atoms which form the Ln_6Al_6 icosahedra. In each icosahedron the *Ln* atoms form two opposite triangles with an Al atom between them. This motif is part of the Ln_3Al alloy structure as seen in Fig. 2.

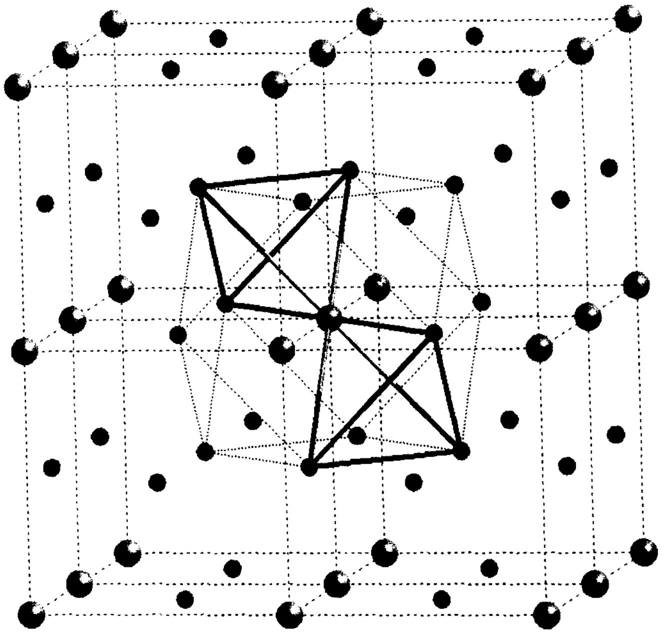

FIG. 2. A view of eight unit cells of the Cu_3Au-type Ln_3Al alloys. Small circles represent *Ln* atoms and large circles represent Al atoms. In the center an Ln_{12} cubooctahedron surrounding an Al atom is depicted. Solid lines connect *Ln* atoms forming two opposite triangles with an Al atom between them. Solid lines also connect these *Ln* atoms with the central Al atom. This array also appears in the cation array of $Ln_3Al_5O_{12}$ garnet, as can be seen in Fig. 1.

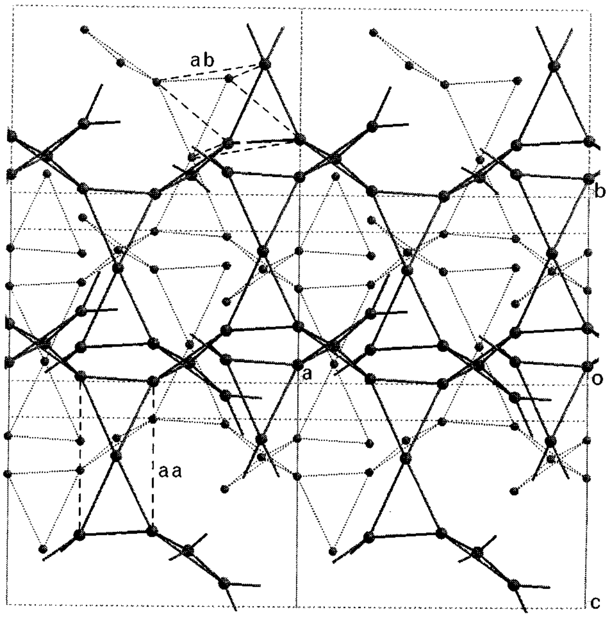

FIG. 3. Perspective view of the subarray of the lanthanide atoms in the garnet compounds. It consists of two interpenetrated identical nets formed by condensed equilateral triangles. The two nets are represented by dotted lines and by continuous lines, respectively. The shortest contacts between the two nets are indicated by *ab*, and the second neighbor distances within one net are indicated by *aa*.

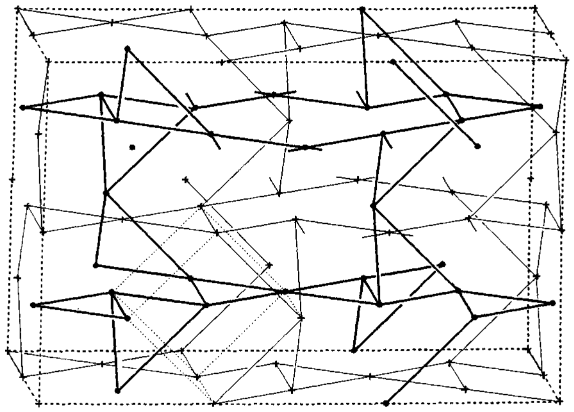

FIG. 4. Perspective view of a bcc net completely decomposed into two similar interpenetrated subnets such as those formed by the lanthanide atoms in garnet-type compounds. The unit cell of the bcc net is indicated with dotted lines at the bottom.

a bcc net in hexagons to reach the *Ln* subarray in the sesquioxide (4). That decomposition uses $(110)_{bcc}$ planes that are common to those proposed in this work and could be regarded as an intermediate step in the solid state reaction that leads to the formation of the garnet structure.

The second type of compound is the perovskite-like $LnAlO_3$ (Ln = La, Ce, Pr, Nd, Sm, Ho). These compounds are not ideal perovskites but they show orthorhombic distortion from the ideal. As is well known, the *AB* cation array in the ABO_3 perovskites adopts the structure of ClCs and, hence, the *Ln* array has a simple cubic structure. Although there is no such structure in the elemental phases of the lanthanides, the simple cubic structure could be thought of as derived from the regularization of a triclinic primitive cell, which can be defined in a bcc array. Such a cell is represented in Fig. 5 and the regularization would lead to

TABLE 1
***Ln–Ln* Distances in $Ln_3Al_5O_{12}$ Garnets**

	$Ln\text{–}Ln_{\text{short}}$	c_{bcc}	$Ln\text{–}Ln_{ab}$	3rd_{bcc}	$Ln\text{–}Ln_{aa}$	4th_{bcc}
Gd	3.71	3.69	5.66	5.73	6.77	6.72
Tb	3.67	3.66	5.61	5.68	6.71	6.67
Dy	3.69	3.62	5.63	5.63	6.73	6.60
Ho	3.67	3.61	5.61	5.60	6.71	6.57
Er	3.66	3.59	5.59	5.57	6.69	6.53
Tm	3.66	3.57	5.59	5.54	6.68	6.50
Yb	3.65	4.04	5.58	6.28	6.67	7.36
Lu	3.65	3.55	5.57	5.51	6.66	6.47

Note. The first column summarizes the shortest *Ln–Ln* distances and the corresponding mean value, $c_{\text{bcc}} = (a + 2d)/3$, in bcc *Ln*. The second column relates the *ab Ln–Ln* distances (see Fig. 3) with the third nearest-neighbors in bcc *Ln*. The third column relates the *aa Ln–Ln* contacts (see Fig. 3) with the fourth nearest-neighbors in bcc *Ln*. All distances are given in Å.

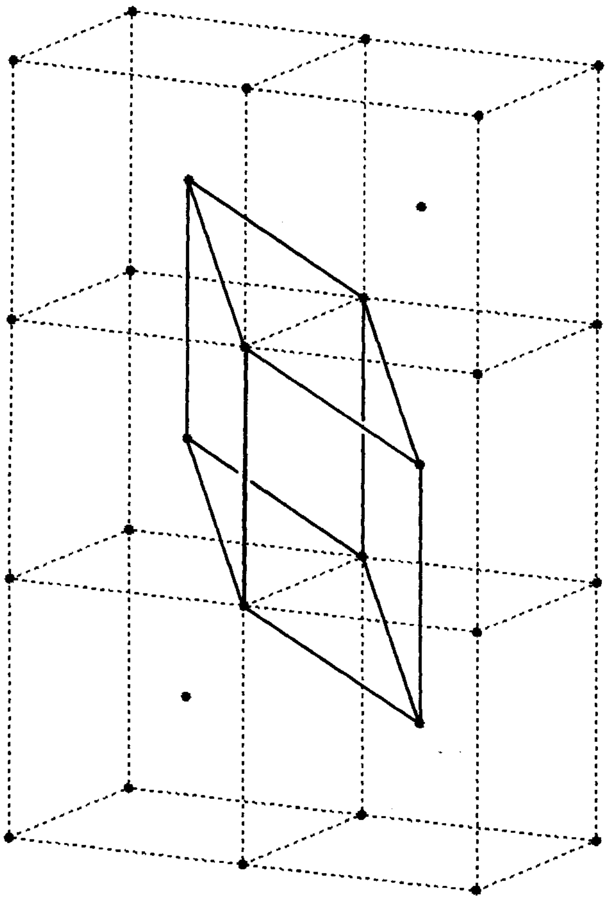

FIG. 5. Irregular primitive cell which can be derived from a bcc array. The regularization of this cell would give rise to the simple cubic array present in the perovskite-like $AlLnO_3$ compounds.

a cubic cell of dimensions $c = (8d + 4a)/12$, where d is the shortest M–M distance in a bcc net and a is the unit cell parameter. The values of c and the experimental values for the $LnAlO_3$ perovskites are compared in Table 2, where it can be seen that deviations are of the order of 2% or less.

TABLE 2

Distances between Lanthanide Atoms (*Ln*–*Ln*) in Al*Ln*O$_3$ Compounds, Compared with the Mean Value of the Edges of the Primitive Cell (Drawn in Fig. 5) Derived from Their bcc Phases (*a* pc-bcc) and with the Parameter *a* of the CsCl-Type Alloys of Formula Al*Ln*

	La	Ce	Pr	Nd	Sm	Ho
Ln–*Ln*	3.79	3.77–3.80	3.76	3.75	3.70–3.78	3.71–3.74
a pc-bcc	3.88	3.75	3.76	3.76	3.71	3.61
a (Al*Ln*)	—	3.86	3.82	3.74	3.74	—

Note. All distances are given in Å.

Another interesting relationship can be established between the $LnAl$ subarray of the $AlLnO_3$ perovskites and the $LnAl$ alloys themselves, which are of the ClCs type. The similarity is not only in topology but also in dimensions. As can be seen in Table 2, the *Ln*–*Ln* distances are similar to the unit cell dimensions of the alloys. Consequently, the molar volumes in both the alloys and the oxides are almost identical, as if the oxygen atoms would be inserted into the net of the alloy without any volume increase. A similar feature was reported for the MSn alloys and the $MSnO_3$ (M = Ca, Sr, Ba) perovskites, which represented new examples of what could be called "real" oxygen-stuffed alloys (10).

CONCLUDING REMARKS

The compounds discussed here represent new examples of how the cation array can be related to the structure of the parent metal. In these cases, an additional relationship can be established: the recognition in the oxides of either the total or the partial structure of the alloys in the Al–*Ln* system. The recognition is complete in the $AlLnO_3$ perovskites and partial in the $Ln_3Al_5O_{12}$ garnets, which show fragments of both Ln_3Al and Al_3Ln alloys. As we have discussed, the *Ln*–Al distances of both alloys are reproduced in the oxides. This feature together with the difficulties of attaining *Ln*–*Ln* distances shorter than those in the metals could force the Al subnet to expand to reproduce the *Ln*–Al and the *Ln*–*Ln* distances in such a way that the metallic aluminum structure is not evident in the compounds.

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REFERENCES

1. A. Vegas, A. Romero, and M. Martínez-Ripoll, *J. Solid State Chem.* **88,** 594 (1990).
2. A. Vegas, A. Romero, and M. Martínez-Ripoll, *Acta Crystallogr. Sect. B* **47,** 17 (1991).
3. A. Vegas and M. Martínez-Ripoll, *Acta Crystallogr. Sect. B* **48,** 747 (1992).
4. A. Ramos-Gallardo and A. Vegas, *J. Solid State Chem.* **119,** 131 (1995).
5. M. O'Keeffe and B. G. Hyde, *in* "Structure and Bonding," Vol. 61, p. 77, Springer-Verlag, Berlin, 1985.
6. A. Ramos-Gallardo and A. Vegas, *Z. Kristallogr.* **210,** 1 (1995).
7. A. Ramos-Gallardo and A. Vegas, *Z. Kristallogr.* **211,** 299 (1996).
8. B. G. Hyde and S. Andersson, "Inorganic Crystal Structures." Wiley, New York, 1989.
9. S. Geller, *Z. Kristallogr.* **125,** 1 (1967).
10. L. A. Martínez-Cruz, A. Ramos-Gallardo, and A. Vegas, *J. Solid State Chem.* **110,** 397 (1994).