Unusual Structural Relaxation for Rare-Earth Impurities in Sapphire: *Ab Initio* Study of Lanthanum

C. Verdozzi,* D. R. Jennison,† P. A. Schultz, M. P. Sears, J. C. Barbour, and B. G. Potter
Sandia National Laboratories, Albuquerque, New Mexico 87185-1413

(Received 4 August 1997)

A first-principles density-functional local density approximation study of substitutional La, using 120-atom supercells of α-Al_2O_3, shows that La assumes a highly displaced position, moving over 0.5 Å from the original Al site. The La-O nearest neighbor distance is much smaller than the sum of standard La^{+3} and O^{-2} ionic radii. This is due to La being more ionic than in its own oxide, and to the role of the 5d shell, as the electron density within the displaced La is quite anisotropic. We discuss the implications for a systematic description of rare-earth ions implanted in sapphire. [S0031-9007(98)06346-7]

PACS numbers: 71.55.Mb, 71.55.Ht

Aluminum oxide, Al_2O_3, is one of the most important ceramics [1] with respect to corrosion, catalysis, and thin film technology. More relevant here, Al_2O_3 is a promising candidate for a new generation of emissive optical materials, making use of isolated impurities in ceramic matrices. With current emissive sources and gain media (SiO_2 optical fibers), low loss and nondispersive light emission relies on the excited states of rare-earth (RE) ions incorporated in homogeneous materials. Future higher communication rates and greater data density will likely depend on new RE-ion hosts where the local environment is manipulated to alter the optical behavior.

Because of large computational requirements, many aspects of these systems lack a detailed understanding at the *ab initio* level. Typically, this is due to (i) the large unit cell of some Al_2O_3 polymorphs; (ii) the length scale (typically nanoscale) of the phenomenon investigated; or (iii) the strongly ionic character of Al_2O_3, causing significant electrostatic forces with any departure from periodicity. An example involves reported *ab initio* calculations of α-Al_2O_3(0001), which use slabs only three oxygen layers thick [2]. On physical grounds, deeper significant relaxations are to be expected due to strong electrostatic forces [3].

An important achievement would be a model to describe and design *a priori* the emissive properties of these materials. A first step is to study RE dopants in homogeneous hosts. We present here an *ab initio* theoretical study of the structural and electronic properties of a La impurity in sapphire (α-Al_2O_3). We find that the local geometry of the La site is grossly different than would be predicted using simple concepts such as ionic radii, and propose a physical explanation for the observation.

Several theoretical papers on RE or transition metal (TM) impurities in alumina [4] used molecular dynamics with semiempirical potentials to provide relaxed atomic coordinates, which in turn yield electrostatic potentials. Crystal field theory (often only as a first order perturbation) then gives energy splittings for Judd-Ofelt [5] analyses of the d-, f-shell optical oscillator strengths. Most calculations predict local relaxations explainable by ionic radii, and in many cases this works well. However, large inaccuracies could result if calibrated potentials are not available from experiment or *ab initio* theory. For example, the structural energies of different ordered phases of bulk alumina have been compared using *ab initio* and semiempirical methods [6]. With the latter, the α phase prevails only after introducing dipolar and quadrupolar polarizability into a compressible ion model. In fact, even a specific functional form for the potential may be an oversimplification [7], and such shortcomings are avoided by density functional treatments of bulk sapphire [6,8]. However, to our knowledge, ours is the first such study of a nearly isolated RE impurity in a ceramic host.

The electronic structure of pure α-Al_2O_3 has been investigated by several methods [6,8–15], but work using the local density approximation (LDA) [6,8,13–14] or generalized-gradient approximation (GGA) [15] is rather recent. Our calculations were performed with the density functional [16] massively parallel code QUEST (quantum electronic structure) [17]. We used the Perdew-Zunger LDA parametrization [18] of the Ceperley-Alder electron gas results [19] and the generalized norm-conserving pseudopotentials of Hamann [20], with cutoff radii sufficiently small as to not affect the results. We did not use GGA for this system because it does not improve geometries and is apparently unimportant for energies [15]. An important core correction [21] was included for La. The atomic bais sets were contracted Gaussians of the "double zeta" plus polarization function type [22]. La had no f bases, justified because the atomic promotion energy to the 1f from the 6s or 5d shells is high (~4 eV) [23]. To achieve near-linear scaling, QUEST employs an algorithm due to Feibelman [24]. Geometric relaxation was done through an iterative Broyden scheme [25], using accurately computed interatomic forces [26].

While scalar relativistic effects are in the pseudopotential, no spin-orbits effects were included because La is highly ionic in Al_2O_3 (see below) and the 5d orbital is only slightly filled. This view is also supported by accurate calculated lattice constants for La_2O_3 (see below), which also justifies the neglect of f bases (evidently compensated by d-polarization functions on the surrounding oxygens, found important for accurate geometries).

Bulk α-Al_2O_3 was found to have interatomic distances within 0.3% of experiment and the electronic density of states agreed well with experimental and theoretical data in the literature. As is typical of LDA, the insulating gap (6.22 eV at the Γ point) is smaller than experiment, here by $\sim$30%, agreeing well with an earlier result of 6.31 eV (see Ref. [8] and discussion therein).

Another test system had a ten-atom Al_2O_3 unit cell with a La impurity substituted for Al. Its purposes were as follows: (i) to produce a small referencing system for Al_2O_3 and La polarization function optimizations, and (ii) to have a sensible initial guess for the possible local lattice expansion around the La ion, expected to be large because of differences in the standard La^{+3} and Al^{+3} ionic radii (1.03 and 0.54 Å, respectively, for sixfold coordination [27]). Calculations showed that for this system (periodically repeated La impurities in a sapphire host) there is a substantial local outwards relaxation around the La atom; this gave a 16% volume expansion for the unit cell together with a less significant reduction of the angle(s) between the primitive vectors (0.3%).

To simulate an isolated La impurity, we used a 120-atom hexagonal supercell, with a central Al replaced by La. The degree of isolation of the impurity is measured by changes in the lattice constants of the relaxed supercell compared with pure Al_2O_3. Isolation is achieved to a good extent: The cell unit vectors increase (maintaining their ratios) by only $\sim$0.6%, thus indicating little interaction. After renormalization for the number of atoms, this expansion is very close to that observed for the small La-containing Al_2O_3 periodic system mentioned above. In addition, comparing the Al_2O_3 120-atom supercell (with one k point) to the ten-atom cell (with 23 k points) showed the total energy per atom and the density of states (DOS) were in excellent agreement, as expected.

The geometry for the relaxed La:Al_2O_3 structure is summarized in Table I with bulk Al_2O_3 for comparison. We denote by X the site of the impurity replacement, having an Al or La ion in Al_2O_3 or La:Al_2O_3, respectively (see Fig. 1). For Al_2O_3, three of the (six) octahedrally coordinated O ions around the $X = $ Al site are at a shorter distance than the remaining three. We denote the two types by O1 and O2. This nomenclature also applies to La:Al_2O_3. In our supercell, the O1 (O2) ions are reciprocally coplanar and lie below (above) the impurity site.

As Table I shows, the insertion of La has a rather dramatic effect on the local structure. At 2.06 Å, the La-O1 distance is *significantly* smaller than the sum of the ionic radii [27]: 1.03 Å (La^{+3}) + 1.38 Å (O^{-2}) = 2.41 Å. La-O1 is also much smaller than the actual separation in the low-temperature structure of La_2O_3 (2.46 Å). In contrast, at 1.85 Å, the A1-O1 distance is in good agreement: 0.54 Å (Al^{+3}) + 1.38 Å (O^{-2}) = 1.92 Å. The possibility that this is an effect of incomplete relaxation was ruled out, since the total energy was minimized also with respect to supercell expansion. The La displacement also alters the position of the O1 ions, whose distance from each other increases by 0.65 Å. However, the distance between the O1 and O2 planes ("X to O1 plane" + "X to O2 plane" in the table) remains constant to a good approximation. In short, the equilibrium position of the La-ion is almost coplanar with the three O1 ions, and its position is strong evidence that its radius is not twice that of Al^{+3}, as expected from the ionic radii difference, but actually is only $\sim$45% larger.

The explanation for this rather unexpected behavior has several factors. The first is the open character of the metal-sublattice structure of sapphire. Along the c axis, Al atoms are arranged in the …Al-Al-void… sequence, and the La substitutional impurity has an Al atom to one side and a void to the other. This causes the La ion to migrate towards the void, away from the opposing Al (see Figs. 2 and 3), in order to minimize the electrostatic La-Al repulsion. However, this argument applies to Al ions as well as substitutional La.

One must still consider what discriminates the two ions. To this end, we performed the following calculations: In the fully relaxed La : Al_2O_3 structure, we removed the La ion and identified the position midway between the La position and that occupied by Al in pure sapphire. We then placed alternatively La and Al in that position (as shown in Figs. 2 and 3). We found that Al and La are both subject to strong restoring forces, but these are *opposite* in sign. Thus, La tends to return to the nearly coplanar position with the three Ol oxygen anions, while Al tends to recover the position in the ideal structure, close to the center of the octahedral void. This clearly indicates that the local host electrostatic potential is *not* the origin of the different behavior of the two ions, but that the result is due to contrasting atomic properties, such as radius (determined by the fractional ionicity) and/or hybridization in the presence of the host potential.

The standard ionic radius of La^{+3} originates in the lattice constants of La oxides and halides. However, the Madelung potential in Al_2O_3 is stronger than in La_2O_3 because the lattice constants are smaller. This must increase the fractional ionicity (and thus decrease the radius) of substitutional La:Al_2O_3 vs La in its own oxide. Rather than resort to atomic electron populations, which are always basis set dependent, we instead focus on the physically observable quantity electron density. Indeed, as seen in Figs. 2 and 3, at distances near the La nucleus the electron density for La in Al_2O_3 is significantly *lower* than for Al (note these are log plots, with darker regions noting lower density). Higher ionicity reduces the radius at which repulsion balances electrostatic forces, thus enabling La to displace in response to the electrostatic gradient of the host.

A second factor is that La possesses a different atomic orbital structure than Al, specifically the presence of a

TABLE I. Local geometry of Al vs substitutional La in Al_2O_3.[a]

	X-O1	X-O2	O1-O1	O2-O2	O1-X-O1 (angle)	O2-X-O2 (angle)	X to O1 plane	X to O2 plane
Al_2O_3 X = Al	1.85	1.96	2.86	2.51	101.43°	79.36°	0.83	1.32
La:Al_2O_3 X = La	2.06	2.47	3.51	2.63	117.10°	64.38°	0.35	1.95

[a] Distances in Å; angles in degrees; for notation, see Fig. 1.

valence d shell. Indeed, when we compare the partial DOS (PDOS) of substitutional La vs Al, we find that the latter has its electron density shared rather evenly between the $3s$ and $3p$ orbitals, while La has over 90% of its density in the $5d$ shell. While the radius of the $5d$ shell is only slightly less than that of the $6s$ orbital, its overlap with adjacent ions, and thus the hard-wall repulsion, is substantially less due to the nodal structure in the angular dependence. In addition, charge in the $5d$ shell can be anisotropic. Upon an examination of the La electron density at the relaxed site or at the site in Fig. 3, we find between 0.1 and 1 bohr from the nucleus over a 50% difference in valence charge between the in-O1-plane vs out-of-plane directions, as also may be seen in the figure. The anisotropy further reduces the energetic cost of being close to and nearly coplanar with the three nearest neighbor oxygen ions, in a site with near C_{3v} symmetry.

Anisotropy can in principle be achieved in Al by promoting electrons from the $3s$ to the $3p$ shell (we observe some promotion as the s and p PDOS areas for Al are about the same). However, atomic tables [23] show the energetic cost of promotion is 3.6 eV per electron, compared with only 0.33–1.1 eV (depending on the atomic state) for $6s$ to $5d$ promotion in La. Thus La has a much greater ability to take advantage of the local electrostatics than does Al. In passing, we note that the relaxation energy (i.e., the energy difference between the final structure and that obtained by substituting La for Al in the perfect lattice) is 4.9 eV, showing the large energy available to alter the La ion. This makes the La-O distance sensibly smaller than the sum of ionic radii.

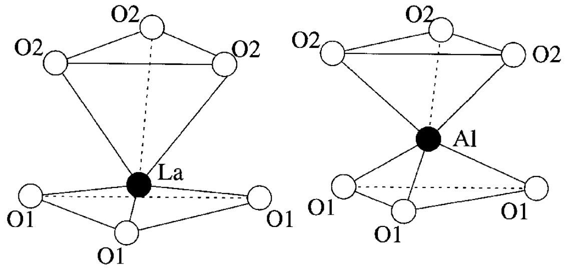

FIG. 1. The position in the octahedral void assumed by Al (normal material) and by the substitutional La impurity. The labels on the oxygen atoms refer to notation used in Table I and the text.

In order to rule out the possibility that our result is caused by errors in the La pseudopotential or basis functions, we also performed calculations on bulk La_2O_3 in the so-called low temperature hexagonal structure. We obtained a LDA lattice constant (a axis) of 3.82 Å (at 0 K), versus the experimental value 3.94 Å (at 300 K). Part of the difference can be ascribed to thermal expansion, part to the LDA, and, in principle, part could be due to the choice of La basis functions. However, our point is that the pseudopotential and basis we use for La give a lattice parameter only 3% smaller than the experimental value; i.e., our conclusions are quantitative to good accuracy. We also note that the charge density near the *relaxed* La position in Al_2O_3 is similar to that near La in La_2O_3—of course, this is not true at the unrelaxed position or the intermediate site of Fig. 3, where it is much lower.

In conclusion, our general arguments concerning fractional ionicity and rehybridization should apply to all RE materials, and therefore all should exhibit the pronounced displacement. Indeed, the literature does reveal a Rutherford backscattering study of Er:Al_2O_3, where a displacement slightly larger than our computed value was found [28], consistent with Er being smaller than La. Since the

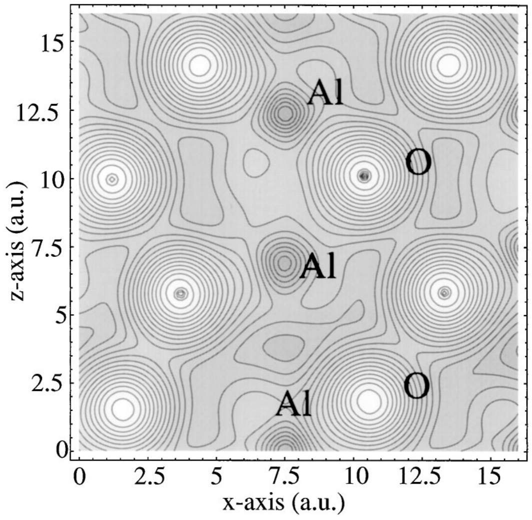

FIG. 2. The logarithm of the electron density for a slice showing an Al atom (center of picture) at a position midway between the normal Al position and the final La position. The force experienced by the Al atom is upward. The x axis is in the O1-Al-O2 plane; the z axis is the crystalline c axis. Darker regions denote lower density.

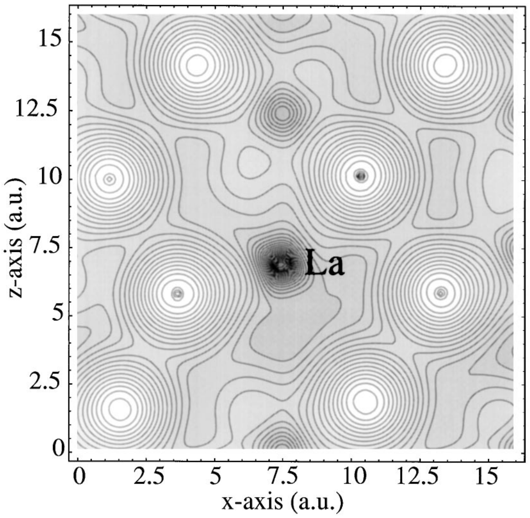

FIG. 3. The same as Fig. 2 except that the center Al atom is replaced by La. The force experienced by the La is downward. Note the greatly reduced electron density and the asymmetry in the La region compared with the center Al in Fig. 2.

s-to-d rehybridization is not available to group IIIA elements, the importance of this factor, in contrast to fractional ionicity, can be tested by experiments comparing groups IIIA and IIIB impurities. In general then, with other than pure compounds, simple models for ionic solids may not produce the correct interactions, unless fractional ionicity and hybridization can change. Details of the impurity site affect not only the atomic energy levels, but also the phonon density of states and phonon-assisted optical transitions, which determine the energy of the emitted photons, the transition probabilities, and the lifetimes of the excited states. Thus, any theoretical treatment of the optical properties of RE impurities would be completely incorrect without knowledge of the highly distorted site found by our calculations.

We thank Roland Stumpf for critical comments. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract No. DE-AC04-94AL85000. This work was partially supported by a Laboratory Directed Research and Development project.

---

[*] Also at IRCSS, The University of Liverpool, P.O. Box 147, Liverpool L69 3BX, United Kingdom. Present address: Department of Physics, University of Edinburgh, Edinburgh EH9 3JZ, United Kingdom.

[†] Author to whom correspondence should be addressed. Electronic address: drjenni@sandia.gov

[1] See, for example, Topical Issue on Science of Alumina [J. Am. Ceram. Soc. **77**, (1994)]; *The Surface Science of Metal Oxides*, by V. E. Henrich and P. A. Cox (Cambridge University Press, Cambridge, England, 1994).

[2] For a review, see M. V. Finnis, J. Phys. Condens. Matter **8**, 5811 (1996).

[3] C. Verdozzi, D. R. Jennison, P. A. Schultz, and M. P. Sears (to be published).

[4] See, for example, M. Wolfs and J. O. Thomas, J. Mater. Chem. **4**, 839 (1994); P. W. Jacobs and E. A. Kotomin, J. Am. Ceram. Soc. **77**, 2505 (1994).

[5] B. R. Judd, Phys. Rev. **127**, 750 (1962); G. S. Ofelt, J. Chem. Phys. **37**, 511 (1962).

[6] M. Wilson, M. Exner, Y.-M. Huang, and M. W. Finnis, Phys. Rev. B **54**, 15 683 (1996).

[7] N. L. Allan and W. C. Mackrodt, Philos. Mag. B **69**, 871 (1994).

[8] W. Y. Ching and Y. N. Xu, J. Am. Ceram. Soc. **77**, 404 (1994); J. C. Boettger, Phys. Rev. B **55**, 750 (1997), and references therein.

[9] I. P. Batra, J. Phys. C **15**, 5399 (1982).

[10] S. Ciraci and I. P. Batra, Phys. Rev. B **28**, 982 (1983).

[11] A. Balzarotti, F. Antonangeli, R. Girlanda, and G. Martino, Phys. Rev. B **29**, 5933 (1984).

[12] M. Causa, R. Dovesi, C. Roetti, E. Kotomin, and V. R. Saunders, Chem. Phys. Lett. **140**, 120 (1987).

[13] J. Guo, D. E. Ellis, and D. J. Lam, Phys. Rev. B **45**, 3204 (1992).

[14] A. Clotet, J. M. Ricart, C. Sousa, and F. Illas, J. Electron Spectrosc. Relat. Phenom. **69**, 65 (1994).

[15] I. Frank, D. Marx, and M. Parrinello, J. Chem. Phys. **104**, 8143 (1996); Y. Yourdshahyan, U. Engberg, L. Bengtsson, B. I. Lundqvist, and B. Hammer, Phys. Rev. B **55**, 8721 (1997).

[16] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964); W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965); see also *Theory of the Inhomogeneous Electron Gas*, edited by S. Lundqvist and N. M. March (Plenum, New York, 1983).

[17] Written and developed by M. P. Sears and P. A. Schultz at Sandia National Laboratories, Alburquerque, NM 87185-1111.

[18] J. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).

[19] D. M. Ceperley and B. J. Alder, Phys. Rev. Lett. **45**, 566 (1980).

[20] D. R. Hamann, Phys. Rev. B **40**, 2980 (1989).

[21] S. G. Louie, S. Froyen, and M. L. Cohen, Phys. Rev. B **26**, 1738 (1982).

[22] Contact P. A. Schultz, Sandia National Laboratories, Albuquerque, NM 87185-1111; paschul@cs.sandia.gov. See also P. J. Feibelman, Phys. Rev. B **38**, 1849 (1988).

[23] C. E. Moore, *Atomic Energy Levels*, Natl. Bur. Stand. (U.S.) Circular No. 467 (U.S. GPO, Washington, DC, 1949).

[24] P. J. Feibelman, Phys. Rev. B **33**, 719 (1986); **35**, 2626 (1987).

[25] D. D. Johnson, Phys. Rev. B **38**, 12 807 (1988).

[26] P. Pulay, Mol. Phys. **17**, 197 (1969).

[27] E. Fluck and K. G. Hellman, *Periodic Table of the Elements* (VCH, Weinheim, 1993) [compiled with IUPAC (1991) data].

[28] E. Alves, M. F. Da Silva, G. N. van den Hoven, A. Polman, A. A. Melo, and J. C. Soares, Nucl. Instrum. Methods Phys. Res. Sect. B **106**, 429 (1995).