

**First-principles study of the orthorhombic CdTiO<sub>3</sub> perovskite**

G. Fabricius\* and A. López García†

*Depto. de Física, Univ. Nacional de La Plata, 1900 La Plata, Argentina*

(Received 18 July 2002; published 31 December 2002)

In this work we perform an *ab initio* study of the CdTiO<sub>3</sub> perovskite in its orthorhombic phase using the FLAPW method. Our calculations help to decide between the different crystallographic structures proposed for this perovskite from x-ray measurements. We compute the electric field gradient tensor (EFG) at Cd site and obtain excellent agreement with available experimental information from a perturbed angular correlation experiment. We study EFG under an isotropic change of volume and show that in this case the widely used “point charge model approximation” to determine EFG works quite well.

DOI: 10.1103/PhysRevB.66.233106

PACS number(s): 77.84.Dy, 61.66.-f, 71.15.Nc

Perovskites materials of the form  $ABO_3$  have been intensively studied last years. In addition to the interest that present the technological applications of ferroelectric materials, perovskites are known to undergo several phase transitions as a function of temperature that make them appealing for theoreticians and experimentalists. The transitions between different structures usually involve very little atomic displacements and are difficult to characterize, requiring some times several experimental techniques. First principles calculations have been playing an increasing role in the understanding of these systems.<sup>1</sup> These studies not only try to give theoretical explanations to the observed phenomena, but usually give valuable information that help in the interpretation of the experimental results.

CdTiO<sub>3</sub> perovskite has been the object of several studies using x-ray diffraction,<sup>2-4</sup> dielectric properties methods,<sup>4-6</sup> infrared spectroscopy,<sup>7</sup> and perturbed angular correction (PAC) technique<sup>8,9</sup> and there have been some difficulties and controversies in determining the symmetry group of its orthorhombic structure at room temperature. In 1957 Kay and Miles established through x-ray measurements that CdTiO<sub>3</sub> perovskite should have orthorhombic symmetry and noncentrosymmetric  $Pbn2_1$  (Ref. 10) space group with a large displacement of Ti atoms along the  $b$  axis.<sup>3</sup> However, the measurement of the electrical properties of CdTiO<sub>3</sub> single crystals could not resolve whether they were ferroelectric or not, then, the displacement of Ti atoms from their symmetric positions couldn't be confirmed.<sup>6</sup> In Ref. 8 Baumvol and co-workers study the EFG at Cd in CdTiO<sub>3</sub> through PAC measurements. Using the point charge model approximation (PCM) to estimate theoretically the EFG, they infer that the structure of the perovskite could not be the one corresponding to  $Pbn2_1$  space group but should be another one with centrosymmetric space group, also considered and discarded by Kay and Miles. Baumvol *et al.* made their arguments based on the asymmetry of EFG tensor, but in fact they obtained a disagreement of about 80% in the absolute value of EFG components. In 1987 Sasaki *et al.*<sup>4</sup> performed new x-ray studies on CdTiO<sub>3</sub>. They obtained that two orthorhombic structures with very similar coordinates and different space groups (centrosymmetric  $Pbnm$  and noncentrosymmetric  $Pbn2_1$ ) fitted equally well the x-ray data. Analyzing some structural and physical properties, they finally argued

that it was more suitable to assign the space group  $Pbnm$  to CdTiO<sub>3</sub>. The main objective of the present work is to clarify this picture, studying from first-principles the electronic properties of the different structures proposed for the CdTiO<sub>3</sub> perovskite.

Another important question that may be learned from this system concerns the correctness of the predictions made by FLAPW and PCM approximation to the EFG tensor at Cd. With PAC technique the EFG tensor at a probe introduced in the solid can be determined,<sup>11</sup> and Cd is one of the most used PAC probes, so, it is of valuable interest to check the different theoretical approaches to the problem of determining EFG at a Cd site. In the PCM the EFG at the probe is usually approached as

$$V_{ij} = (1 - \gamma_\infty) V_{ij}^{\text{latt}} \quad (1)$$

where  $V_{ij}^{\text{latt}}$  is the EFG produced by the valence charges located as point charges at the ions positions. In this approximation the only effect of the probe is to antishield the lattice contribution through the Sternheimer antishielding factor,<sup>12</sup> that for Cd is usually taken as  $\gamma_\infty = -29.27$ .<sup>13</sup> PCM has been extensively used to predict EFG at Cd sites in perovskites and oxides<sup>14-17</sup> but calculations at the *ab initio* level are rare in these systems because Cd usually enters the solid as impurity and this introduces several complications, as the effect of atomic relaxations, for example.<sup>18</sup> In the case of CdTiO<sub>3</sub> perovskite, Cd is one of the constituents of the system, so accurate *ab initio* calculations can be performed and used to check the validity of PCM approximation.

The first-principles calculations were performed with the WIEN97 implementation of the full-potential linearized-augmented-plane-wave (FLAPW) method developed by Blaha *et al.*<sup>19</sup> We use the generalized gradient approximation (GGA) to describe the exchange correlation potential in the parametrization of Perdew *et al.*<sup>20</sup> The size of the basis set in these calculations is controlled by the parameter  $RK_{\text{max}}$  that we fixed in the value of 8. The atomic sphere radii were chosen as 1.06, 0.90 and 0.85 Å for Cd, Ti and O atoms respectively. Integrations in reciprocal space were performed with the tetrahedron method using 18 and 36  $k$  points in the

TABLE I. Absolute value of forces on inequivalent atoms (F) in eV/Å component of largest absolute value of the EFG tensor ( $V_{33}$ ) in  $10^{21}$  V/m<sup>2</sup> and asymmetry parameter ( $\eta$ ) calculated in the present work compared with PAC experiment.

	F(Cd)	F(Ti)	F(O1)	F(O2)	F(O3)	$V_{33}$	$\eta$
<i>Pbn2</i> <sub>1</sub> : Ref. 3	1.84	3.43	3.85	1.04	3.63	+10.00	0.80
<i>Pbnm</i> : Ref. 4	0.03	0.00	0.05	0.05		-5.10	0.42
<i>Pbn2</i> <sub>1</sub> : Ref. 4	0.03	0.10	0.41	0.45	0.54	-5.14	0.42
PAC exp. (Ref. 8)						$5.41 \pm 0.80$	$0.407 \pm 0.008$

irreducible first Brillouin zone for *Pbnm* and *Pbn2*<sub>1</sub> structures respectively. The unit cells have 20 atoms containing five molecules of CdTiO<sub>3</sub>. In the case of *Pbnm* structure there are four inequivalent atoms in the cell: Cd( $x_{Cd}, y_{Cd}, \frac{1}{4}$ ), Ti( $\frac{1}{2}, 0, 0$ ), O1( $x_{O1}, y_{O1}, \frac{1}{4}$ ), and O2( $x_{O2}, y_{O2}, z_{O2}$ ), while for *Pbn2*<sub>1</sub> structure there are five inequivalent atoms: Cd( $x_{Cd}, y_{Cd}, \frac{1}{4}$ ), Ti( $x_{Ti}, y_{Ti}, z_{Ti}$ ), O1( $x_{O1}, y_{O1}, z_{O1}$ ), O2( $x_{O2}, y_{O2}, z_{O2}$ ), and O3( $x_{O3}, y_{O3}, z_{O3}$ ). Once self-consistency of the potential is achieved the  $V_{ij}$  components of the EFG tensor are computed from the lattice harmonic expansion of the self-consistent potential.<sup>21</sup> The EFG tensor is then diagonalized and it is expressed in terms of its greatest absolute value component  $V_{33}$  and the asymmetry parameter  $\eta = (V_{22} - V_{11})/V_{33}$ , where  $V_{ii}$  are the components of the diagonalized tensor that are ordered such that  $|V_{33}| > |V_{22}| > |V_{11}|$ .

In Table I we show the results of our FLAPW calculations performed for the different structures reported in the literature compared with the PAC determination of  $|V_{33}|$  and  $\eta$ . We see that the huge value obtained for the forces in the case of *Pbn2*<sub>1</sub> structure of Ref. 3 and the poor agreement of  $V_{33}$  and  $\eta$  with experiment lead us to discard this structure as the stable one for CdTiO<sub>3</sub> perovskite. In the case of structures of Ref. 4, we see that for both of them we obtained  $V_{33}$  and  $\eta$  in excellent agreement with the experimental result of Baumvol *et al.*<sup>8</sup> The forces obtained for these structures are much smaller than those obtained for *Pbn2*<sub>1</sub> structure of Ref. 3 but the ones on oxygen atoms for *Pbn2*<sub>1</sub> structure of Ref. 4 are still too big to be attributed to the precision of our calculations. So, in order to check the stability of structures of Ref. 4 in the frame of FLAPW calculations, we have relaxed both structures (keeping fixed the lattice parameters at their experimental values) until forces on every atom are below a tolerance value taken as 0.01 eV/Å. These relaxation processes involve the variation of the 7 and 14 independent coordinates that define *Pbnm* and *Pbn2*<sub>1</sub> structures respectively, and we have performed them following a Newton damped scheme.<sup>22</sup> At the end of the relaxations we obtained that both structures relaxed to the same *Pbnm* structure within a tolerance in distances of 0.01 Å. The finally obtained *Pbnm* structure was very similar to the one proposed by Sasaki *et al.*, as expected, due to the small forces previously obtained for this structure shown in Table I. So, our calculations indicate that *Pbn2*<sub>1</sub> structure is not stable and confirm the assignation of *Pbnm* as the space group of CdTiO<sub>3</sub> perovskite that was suggested in Ref. 4. The fact that

x-ray data from Ref. 4 are also adjusted quite well by a non-centrosymmetric structure with oxygens O2 and O3 that slightly appart from their corresponding symmetric positions in *Pbnm* structure may indicate the presence of a soft mode in *Pbnm* structure involving those displacements. A future study of the phonons in the *Pbnm* structure would be valuable in order to check this hypothesis.

As was mentioned, Baumvol *et al.* analyzing the asymmetry of the EFG tensor with the point charge model supposed CdTiO<sub>3</sub> should have a centrosymmetric space group, but in fact they obtained  $V_{33}$  larger than experiment, at least, in 80%. In effect, the discrepancy in  $V_{33}$  would be *only* about 80% assuming the same sign for PCM prediction and experimental value, and they attributed this discrepancy to a failure of PCM to account for a supposed existing covalent contribution to EFG at Cd in this system. But the sign of  $V_{33}$  predicted by Baumvol is opposite to the one that emerges from FLAPW calculations. The point is that they used coordinates of a centrosymmetric structure studied in Ref. 3. If the coordinates obtained later by Sasaki *et al.*<sup>4</sup> are used in the PCM calculations,  $V_{33} = -4.41$  and  $\eta = 0.45$  are obtained in fairly good agreement with experiment and FLAPW calculations. In order to inspect further this agreement between PCM and FLAPW predictions to EFG tensor, we perform FLAPW calculations for an isotropic change of volume of the *Pbnm* structure. For each volume considered we relaxed the internal coordinates and evaluate EFG tensor at the relaxed coordinates. The change is isotropic in the sense that we hold the relations  $a/b$  and  $a/c$  fixed in the experimental ratios of Ref. 4. The results are shown in Table II. Both EFG estimations predict an increase of  $V_{33}$  and  $\eta$  with compression and also an increase of the angle between  $V_{33}$  direction and  $x$  axis. PCM not only predicts the same tendency as FLAPW, but also the absolute values are in fairly good agreement. However, the agreement of  $V_{33}$  and especially  $\eta$  seems to be better for larger Cd-O distances where covalency between Cd and oxygen is smaller. In Ref. 15, using PCM to compare with several PAC measurements in oxides, the authors obtained empirically that when Cd-O bond is larger than 2.1 Å a good agreement between predictions and experiment is found. The results of Table II suggest that the previous affirmation could be generalized including perovskites, since the agreement of PCM with FLAPW begins to worsen when  $d_{nn}(\text{Cd-O})$  approaches this value.

In their PAC study of CdTiO<sub>3</sub> as a function of temperature, Baumvol *et al.* obtained that  $V_{33}$  and  $\eta$  increase when  $T$

TABLE II. Electric field gradients as a function of an isotropic change of volume for the  $Pbnm$  structure of  $CdTiO_3$  perovskite. PCM calculations were performed on the FLAPW-relaxed structures.  $V/V_0$  is the relation between volumes taken in our calculations and those of Ref. 4,  $d_{nn}(\text{Cd-O})$  (in Å) is the nearest-neighbor Cd-O distance.  $V_{33}$  and  $\eta$ , as in Table I.

$V/V_0$	$d_{nn}(\text{Cd-O})$	FLAPW			PCM		
		$V_{33}$	$\eta$	$V_{33}$ direction	$V_{33}$	$\eta$	$V_{33}$ direction
0.913	2.18	-5.63	0.49	(0.759, 0.651, 0)	-4.67	0.59	(0.773, 0.634, 0)
0.956	2.21	-5.33	0.44	(0.772, 0.636, 0)	-4.53	0.52	(0.778, 0.629, 0)
1.000	2.25	-5.04	0.40	(0.787, 0.617, 0)	-4.35	0.47	(0.784, 0.620, 0)
1.046	2.28	-4.82	0.40	(0.807, 0.591, 0)	-4.21	0.45	(0.795, 0.607, 0)
1.093	2.31	-4.62	0.38	(0.829, 0.560, 0)	-4.07	0.41	(0.809, 0.587, 0)

decreases. This confirms the tendency predicted in our calculations assuming a positive thermal expansion coefficient for  $CdTiO_3$ . The augment of  $\eta$  with pressure may be explained because the distortion of the perovskite structure also increases with pressure. This can be seen by looking at Table III where we show the behavior of three parameters defined in Ref. 4 to characterize the distortion of this and other perovskites. For a cubic perovskite  $t_{\text{obs}}=1$ ,  $\phi_{ab}=180^\circ$  and  $\phi_{bc}=90^\circ$ , and when larger is the separation from these values, larger is the distortion of the structure and the tilting of the octahedra. We have obtained that the mentioned parameters vary almost linearly for an isotropic change of volume of  $CdTiO_3$  perovskite.

Even when in this study we keep fixed the  $a/b$  and  $a/c$  relations, and so we do not obtain an unconstrained energy vs volume dependence, it is interesting to look at this  $E(V)$  curve compared with the one of the cubic phase (see Fig. 1). The high energy difference obtained between both phases [two orders of magnitude larger than the one obtained for the same phases in  $BaTiO_3$  (Ref. 23)] may explain why the transition to cubic  $CdTiO_3$  has not been reported.<sup>24</sup> In fact, perovskites that crystallize in an orthorhombic  $Pbnm$  structure at room temperature, such as  $CaTiO_3$ ,  $SrZrO_3$ , and  $SrHfO_3$ , undergo three transitions when the temperature is increased: orthorhombic ( $Pbnm$ )  $\rightarrow$  orthorhombic ( $Cmcm$ )  $\rightarrow$  tetragonal ( $I4/mcm$ )  $\rightarrow$  cubic.<sup>25-27</sup> For the case of  $SrHfO_3$  perovskite, for example, the transitions occur for temperatures

TABLE III. Parameters showing the distortion in  $CdTiO_3$  perovskite as a function of an isotropic change of volume. The observed tolerance factor ( $t_{\text{obs}}$ ) and the tilting angles of the octahedra in  $ab$  plane ( $\phi_{ab}$ ) and  $bc$  plane ( $\phi_{bc}$ ) as defined in Ref. 4.  $t_{\text{obs}} = \langle \text{Cd-O} \rangle / (\sqrt{2} \langle \text{Ti-O} \rangle)$ , where  $\langle \text{Cd-O} \rangle$  and  $\langle \text{Ti-O} \rangle$  are the mean interatomic distances with twelve and six coordination for Cd and Ti sites, respectively.

$V/V_0$	$t_{\text{obs}}$	$\phi_{ab}$	$\phi_{bc}$
0.913	0.9759	141.52	105.20
0.956	0.9765	142.18	105.11
1.000	0.9772	142.87	104.97
1.046	0.9777	143.53	104.81
1.093	0.9783	144.24	104.66

around 870, 1000, and 1360 K. As far as we know, no structural study of  $CdTiO_3$  at high temperature has been performed. Moreover in PAC studies of orthorhombic  $CdTiO_3$  up to 1270 K no signature of any phase transition has been reported.<sup>9</sup> In a previous study on  $SrHfO_3$  (Ref. 28) a difference of 0.27 eV has been obtained between orthorhombic ( $Pbnm$ ) and cubic structures. Thus looking at the 0.8 eV obtained in the present work for  $CdTiO_3$  we would expect the transition to the cubic phase, if present, to occur at very high temperature. Future experimental work on  $CdTiO_3$  at high temperatures would be valuable to check this prediction.

In summary our calculations help to decide between the proposed structures for orthorhombic  $CdTiO_3$  perovskite. We have obtained that within the precision of our FLAPW calculations the proposed  $Pbnm$  structure from Ref. 4 is stable while  $Pbn2_1$  is not. We have obtained very good

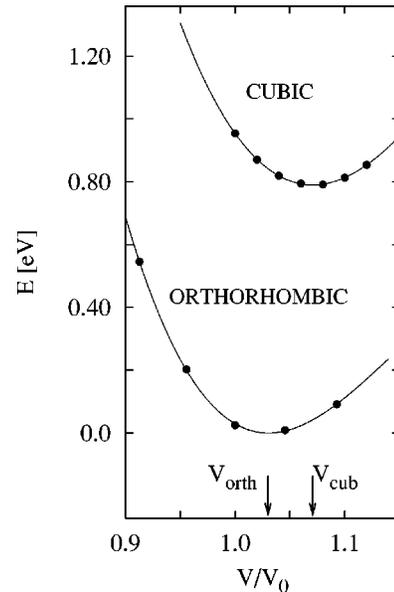


FIG. 1. Energy vs volume for cubic and orthorhombic phases of  $CdTiO_3$  perovskite. Energy is referred to the minimum obtained for the orthorhombic phase, and volume is in terms of the experimental volume of the orthorhombic phase  $V_0$  (Ref. 4). Arrows indicate the positions of the minima of the plotted curves. Full circles: calculated points, lines: cubic fit.

agreement between the calculated EFG and experiment and have shown that PCM approximation works quite well in this case. However, care should be taken when applying PCM to other systems with lower Cd-O bond, since the agreement seems to worsen in this direction. Our energy calculations

suggest that the transition to the cubic phase, if present, would take place at quite high temperature.

This work was supported by CONICET and *Fundación Antorchas*, Argentina. We want to acknowledge Dra. P. de la Presa for fruitful discussions.

\*Electronic address: fabriciu@venus.fisica.unlp.edu.ar

†Electronic address: abeti@venus.fisica.unlp.edu.ar

<sup>1</sup>D. Vanderbilt, *Curr. Opin. Solid State Mater.* **2**, 701 (1997).

<sup>2</sup>H. D. Megaw, *Proc. Phys. Soc. London* **58**, 133 (1946).

<sup>3</sup>H. F. Kay and J. L. Miles, *Acta Crystallogr.* **10**, 213 (1957).

<sup>4</sup>S. Sasaki, C. T. Prewitt, J. D. Bass, and W. Schulze, *Acta Crystallogr.* **43**, 1668 (1987).

<sup>5</sup>G. Martin and E. Heugenbarth, *Phys. Status Solidi* **18**, K151 (1973).

<sup>6</sup>M. L. Sholokhovich, O. P. Kramarov, B. F. Proskuryakov, and E. I. Éknadiosyants, *Sov. Phys. Crystallogr.* **13**, 967 (1969).

<sup>7</sup>A. S. Knyazev, V. P. Zakharov, and Yu. M. Poplavko, *Opt. Spectrosc.* **36**, 950 (1974).

<sup>8</sup>I. J. R. Baumvol, F. C. Zawislak, R. N. Saxena, and L. C. Jahnel, *J. Phys. Chem. Solids* **39**, 175 (1978).

<sup>9</sup>G. L. Catchen, S. J. Wukitch, D. M. Spaar and M. Blaszkiewicz, *Phys. Rev. B* **42**, 1885 (1990).

<sup>10</sup>In fact in Ref. 3 the space group is reported as  $Pc2_1n$ , but we use here  $Pbn2_1$  as in Ref. 4.

<sup>11</sup>H. Frauenfelder and R. M. Steffen, in *Alfa, Beta and Gamma Ray Spectroscopy*, edited by K. Siegbahn (North Holland, Amsterdam, 1965), p. 997.

<sup>12</sup>R. M. Sternheimer, *Phys. Rev.* **80**, 102 (1950).

<sup>13</sup>F. D. Feiock and W. R. Johnson, *Phys. Rev.* **187**, 39 (1969).

<sup>14</sup>M. Forker, A. Hammesfahr, A. López García, and B. Wolbeck, *Phys. Rev. B* **7**, 1039 (1973).

<sup>15</sup>D. Wiarda, M. Uhrmacher, A. Bartos, and K. P. Lieb, *J. Phys.: Condens. Matter* **5**, 4111 (1993).

<sup>16</sup>R. N. Attili, M. Uhrmacher, K. P. Lieb, L. Ziegeler, M. Mekata, and E. Schwarzmann, *Phys. Rev. B* **53**, 600 (1996).

<sup>17</sup>R. Dogra, A. C. Junqueira, R. N. Saxena, A. W. Carbonari, J. Mestnik-Filho, and M. Moralles, *Phys. Rev. B* **63**, 224104 (2001).

<sup>18</sup>L. A. Errico, G. Fabricius, M. Rentería, P. de la Presa, and M. Forker, *Phys. Rev. Lett.* **89**, 055503 (2002).

<sup>19</sup>P. Blaha, K. Schwarz, P. Dufek, and J. Luitz, WIEN97, Vienna University of Technology, 1997. Improved and updated Unix version of the original copyrighted Wien-code, which was published by P. Blaha, K. Schwarz, P. I. Sorantin, and S. B. Trickey, *Comput. Phys. Commun.* **59**, 399 (1990).

<sup>20</sup>J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (1996).

<sup>21</sup>For a detailed description of the formalism used to compute EFG tensor see, for example, K. Schwarz and P. H. Dederichs, *Phys. Rev. B* **37**, 2792 (1988); K. Schwarz, C. Ambrosch-Draxl, and P. Blaha, *ibid.* **42**, 2051 (1990).

<sup>22</sup>B. Kohler, S. Wilker, M. Scheffler, R. Kouba, and C. Ambrosch-Draxl, *Comput. Phys. Commun.* **94**, 31 (1996).

<sup>23</sup>J. Íñiguez, J. B. Neaton, and D. Vanderbilt, *Proceedings of Fundamental Physics of Ferroelectrics, 2002*, edited by R. Cohen and T. Egami (AIP, Melville, 2002).

<sup>24</sup>Note that this argument is not affected by the use of a constrained energy since it is an upper bound, so the  $E_{\text{cub}}-E_{\text{orth}}$  energy difference is a lower bound.

<sup>25</sup>S. A. T. Redfern, *J. Phys.: Condens. Matter* **8**, 8267 (1996).

<sup>26</sup>B. J. Kennedy, C. J. Howard, and B. C. Chakoumakos, *Phys. Rev. B* **59**, 4023 (1999).

<sup>27</sup>B. J. Kennedy, C. J. Howard, and B. C. Chakoumakos, *Phys. Rev. B* **60**, 2972 (1999).

<sup>28</sup>G. Fabricius *et al.* (unpublished).