Anisotropic Relaxations Introduced by Cd Impurities in Rutile TiO_2: First-Principles Calculations and Experimental Support

L. A. Errico, G. Fabricius, and M. Rentería*
Departamento de Física, Facultad de Ciencias Exactas, Universidad Nacional de La Plata, C.C. No. 67, 1900 La Plata, Argentina

P. de la Presa and M. Forker
Institut für Strahlen- und Kernphysik, Universität Bonn, Nussallee 14-16, 53115 Bonn, Germany
(Received 8 April 2002; published 15 July 2002)

We present an *ab initio* study of the relaxations introduced in TiO_2 when a Cd impurity substitutes a Ti atom and an experimental test of this calculation by a perturbed-angular-correlation (PAC) measurement of the orientation of the electric-field gradient (EFG) tensor at the Cd site. The *ab initio* calculation predicts strong anisotropic relaxations of the nearest oxygen neighbors of the impurity and a change of the orientation of the largest EFG tensor component, V_{33}, from the [001] to the [110] direction upon substitution of a Ti atom by a Cd impurity. The last prediction is confirmed by the PAC experiment that shows that V_{33} at the Cd site is parallel to either the [110] or the $[1\bar{1}0]$ crystal axis.

DOI: 10.1103/PhysRevLett.89.055503 PACS numbers: 61.72.Ww, 71.55.Ht, 76.80.+y

Metal impurities in oxides are a challenging problem not only from a fundamental point of view. A reliable calculation of impurity properties such as, e.g., their energy levels in semiconductor oxides is also of great technological importance. Impurities introduce structural atomic relaxations in the host and modify the electronic structure of the system, and it is the interplay of these two effects which makes an adequate theoretical description very difficult. Recently, there have been several attempts to deal with this problem at the *ab initio* level [1,2].

Experimental tests of the *ab initio* predictions are of fundamental importance for the evaluation of models of impurity-induced relaxations. The structural relaxations modify the local electron distribution at the impurity site. A quantity reflecting this distribution is the electric-field gradient (EFG). As the EFG decreases with $1/r^3$ from the producing charge density, it is very "short-sighted" and therefore particularly sensitive to slight local changes. Consequently, the EFG at the impurity site carries information on the relaxations induced by the impurity, and its experimental value may serve as a test of the *ab initio* calculations. The EFG can be determined by a measurement of its electric hyperfine interaction with a quadrupole moment of the impurity nucleus.

In this paper, we present an *ab initio* calculation of the relaxations at Cd impurities on substitutional Ti sites in TiO_2 and the experimental test of this calculation by a measurement of the EFG tensor experienced by the Cd impurities. This particular host (TiO_2)-impurity (Cd) combination was suggested mainly by two aspects. First, strength, symmetry, and orientation of the EFG tensor at the Ti nuclei in the rutile structure of pure TiO_2 are known from previous NMR measurements of the ^{49}Ti quadrupole interaction in single crystals [3]. *Ab initio* calculations [4] are in agreement with this experimental result. Second, ^{111}Cd is one of the most favorable probe nuclei for perturbed-angular-correlation (PAC) experiments and when introduced as an impurity into TiO_2 is known to reside on substitutional Ti sites. PAC is a hyperfine spectroscopic technique that can be applied at very low probe concentrations and is therefore particularly well suited for the investigation of the EFG at isolated impurities. Strength (in terms of the absolute value of the largest principal-axis component, V_{33}) and symmetry of the EFG tensor of ^{111}Cd on Ti sites in TiO_2 have been measured previously by ^{111}Cd PAC in polycrystalline TiO_2 [5,6].

Recently, the EFG of Cd in TiO_2 has been calculated by Sato *et al.* [7] imposing the constraint of isotropic relaxations of the nearest oxygen neighbors and by some of us without this constraint [8]. Although the absolute value of V_{33} provided by experiment is fairly well reproduced, the results of both calculations differ considerably: (i) Opposite signs are predicted and (ii) according to our calculation the substitution of Ti by Cd should change the EFG orientation from the [001] direction of pure TiO_2 to the [110] direction while, according to Sato *et al.*, the [001] direction is not affected. These two approaches to the problem of a Cd impurity in TiO_2 have two shortcomings: (i) The size of the supercell (SC) considered in both calculations (12 atoms) was very small for a dilute impurity calculation, and (ii) the charge state of the impurity was not taken into account in a self-consistent way. In the present work, we have removed both shortcomings by using much bigger SCs and considering different impurity charge states in a fully self-consistent way.

The first-principles calculations were performed with the WIEN97 implementation of the full-potential linearized-augmented-plane-wave (FLAPW) method [9], which has been successfully used to determine the EFG in many compounds [2,10]. We worked in local density approximation [11]. We have considered a $2 \times 2 \times 3$ supercell of 72 atoms consisting of twelve unit cells of TiO_2 (see Fig. 1),

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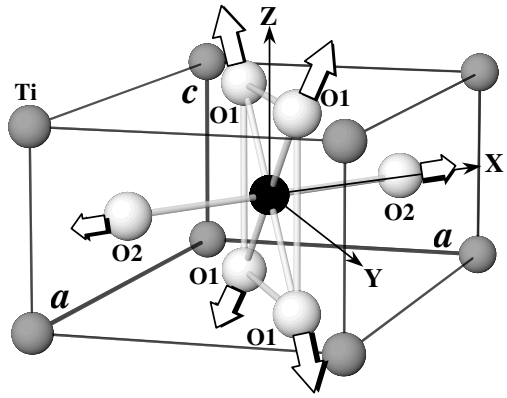

FIG. 1. Unit cell of rutile TiO_2. All the results discussed in this article refer to the indicated axes system, assuming that Cd replaces the black Ti atom.

where one of the 24 titanium atoms is replaced by a Cd atom. Each Cd atom is therefore almost equidistant from its Cd images at a distance of around 9 Å. Substitution of a Ti by a Cd atom makes the resulting system metallic because of the lack of two electrons to fill up the p-O band. It is a question of central importance whether the real system we want to describe provides the lacking electrons (via an oxygen vacancy, for example) or not. In this Letter, we present the results of calculations assuming (a) that extra electrons are not available (neutral impurity state: Cd^0), and (b) that the system somehow provides the lacking two electrons (charged impurity state: Cd^-). In the situation (a), we use the described SC performing calculations on a metallic system. To describe situation (b), we add two electrons to the SC that we compensate with a homogeneous positive background in order to have a neutral cell to compute total energy and forces [$Cd^-(2e)$]. We have also simulated situation (b) by replacing the two most distant oxygen atoms from Cd by two fluorine atoms in order to provide the lacking two electrons without introducing any artificial background [Cd^-(fluorine)].

The value of the parameter $RK_{\max}$ [12], which controls the size of the basis set, was set to 6, and we introduced local orbitals (LO) to include Ti-3s and 3p, O-2s and Cd-4p orbitals. Integrations in reciprocal space were performed using the tetrahedron method taking eight k-points in the irreducible Brillouin zone for the metallic system (a), and two k-points for the nonmetallic ones (b). Once self-consistency of the potential was achieved, the forces were computed [13], the ions were displaced [14], and new positions for Cd neighbors were obtained. The procedure was repeated until the forces on the ions were below 0.025 eV/Å. At the relaxed structure, the V_{ij} elements of the EFG tensor were obtained from the V_{2M} components of the lattice harmonic expansion of the self-consistent potential [15]. We have assumed that relaxations preserve the point-group symmetry of the SC, which restricts O1 and O2 displacements to the **YZ** plane and the **X** axis direction, respectively (see Fig. 1). In order to check the stability of the solution obtained, at the end of the relaxation process we performed new calculations with O1 and O2 atoms displaced from their symmetry positions and verified that this solution is a minimum.

In Table I we show the results for the relaxation of the six nearest oxygen neighbors of the Cd impurity. We see that for both impurity charge states the relaxations are quite anisotropic, with the Cd-O1 distance bigger than the Cd-O2 distance, opposite to the initial unrelaxed structure. This conclusion contradicts the assumptions of previous studies of this system [5,7] and confirms the tendency predicted in the first calculation performed by some of us with a much smaller SC [8]. Anisotropy in the relaxations of the nearest oxygen neighbors of the Cd impurity can be understood by inspection of Fig. 2. Stretching of Cd-O2 bond implies a considerable shortening in Ti-O2 bonds. However, stretching of Cd-O1 bond affects the Ti-O1 bonds not so much, since the structure is more open in this direction. So, at the end of the relaxation, the Cd-O1 bond stretches almost twice as much as the Cd-O2 bond. Relaxations and EFGs are very similar for the two ways of simulating the charged state of the impurity indicating that both approaches are well suited to deal with this problem. These results for EFG agree reasonably well with available

TABLE I. Distances from the Cd impurity to its nearest neighbors (in Å) and the EFG tensor principal components at the Cd site, V_{ii} (in 10^{21} V/m^2), for the relaxed structures of the different systems considered in our calculation compared with experiments and the calculation of Sato *et al.* $\eta = (V_{11} - V_{22})/V_{33}$ ($|V_{33}| > |V_{22}| > |V_{11}|$). In the last row, distances and EFG tensor refer to the Ti site in pure TiO_2. $Q = 0.83b$ ($Q = 0.24b$) was used to calculate V_{33} from the experimental quadrupole coupling constant ν_Q at $^{111}Cd(^{49}Ti)$ sites.

	d(Cd-O1)	d(Cd-O2)	V_{XX}	V_{YY}	V_{ZZ}	V_{33}	V_{33} direction	η
Cd^0	2.15	2.11	−7.16	+6.82	+0.34	−7.16	**X**	0.91
$Cd^-(2e)$	2.18	2.11	−2.87	+4.55	−1.68	+4.55	**Y**	0.26
Cd^-(fluorine)	2.19	2.12	−2.46	+4.10	−1.63	+4.10	**Y**	0.20
Expt. (single crystal)						5.34(1)	**X** or **Y**	0.18(1)
Expt. (polycrystal) [5,6]						5.23(5)/5.34(2)	···	0.18(1)/0.18(1)
Calc. [7]	2.06	2.10	+1.54	+3.56	−5.09	−5.09	**Z**	0.39
Expt. (pure TiO_2 [3]	1.94	1.98				2.2(1)	**Z**	0.19(1)

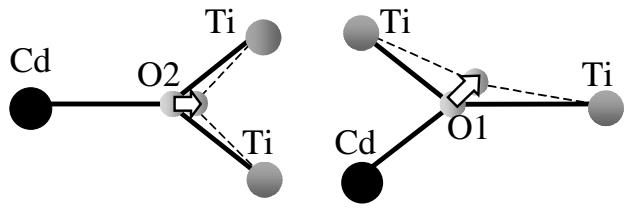

FIG. 2. Planes **XZ** and **YZ** (see Fig. 1) containing O2 and O1 atoms, respectively, with their neighbors. The arrows indicate the displacement of the oxygen atoms from the unrelaxed to the final relaxed positions. The size of the relaxation has been duplicated in order to better visualize the effect.

experimental information [5,6] and are very different from the ones obtained for the neutral state of the impurity, Cd^0. The huge difference obtained in the V_{ii} components for the two impurity charge states is mainly due to the filling of the impurity state at the Fermi level which has an important component of Cd-d_{yz} character [16]. The high η value obtained for Cd^0 is too far from experimental findings suggesting that Cd as an impurity in TiO_2 is in a charged state. The results obtained for $Cd^-(2e)$ changes very slightly when the coordinates of atoms beyond the Cd-nearest neighbors are relaxed (see Table II).

In addition, we also performed FLAPW calculations for the system $Cd^-(2e)$ imposing the constraint of isotropic relaxations of O1 and O2 atoms and obtained V_{33} pointing in [001] direction and a high η value of 0.91 confirming for a converged-size SC that an isotropic relaxation is not consistent with the available experimental data.

To check the accuracy and convergence of our results, we have performed additional calculations at the relaxed structure of case $Cd^-(2e)$ with $R_C = 2.5$ Å considering $RK_{\max} = 7$, including LO for Cd-4d orbitals, increasing the mesh in $\vec{k}$ space, using generalized gradient approximation [17] for exchange-correlation potential and also considering $2 \times 2 \times 2$ and $2 \times 2 \times 4$ SCs. These checks show that d(Cd-O1) and d(Cd-O2) are converged within 0.01 Å and V_{33} and η within 0.5×10^{21} V/m^2 and 0.1, respectively. Details will be presented in a forthcoming paper [16].

In order to check the change in orientation of V_{33} from the **Z** to the **Y** direction upon substitution of a Ti atom by a Cd impurity, we performed PAC experiments in TiO_2 single crystals with the ^{111}Cd probe. The PAC technique measures the probability $W(\mathbf{k}_1, \mathbf{k}_2, t)$ to detect the second γ-ray of a nuclear-decay γ-γ cascade at the direction $\mathbf{k}_2(\theta_2, \phi_2)$ after a time t the first γ-ray was detected at the direction $\mathbf{k}_1(\theta_1, \phi_1)$, where θ_i and ϕ_i describe the propagation direction of γ_1 and γ_2 with respect to a chosen quantization axis. The angular correlation may be modulated in time by hyperfine interactions which induce transitions between the m states of the intermediate level of the cascade, changing their population distribution (relative to γ_1) and thus the angular distribution of γ_2. The correlation function $W(\mathbf{k}_1, \mathbf{k}_2, t)$ therefore carries information on the strength, symmetry, and time dependence of the hyperfine field and is sensitive to the orientation of the interaction with respect to $\mathbf{k}_1$ and $\mathbf{k}_2$.

TABLE II. Results of the different relaxations performed for system $Cd^-(2e)$. N_A is the number of atoms (within a radius R_C from Cd) that relax in each case. All units as in Table I.

R_C	N_A	d(Cd-O1)	d(Cd-O2)	V_{XX}	V_{YY}	V_{ZZ}	η
2.5	6	2.185	2.111	−2.87	+4.55	−1.68	0.26
4.0	24	2.176	2.104	−3.25	+4.99	−1.74	0.30
4.6	42	2.187	2.116	−3.17	+4.86	−1.69	0.30

The orientation dependence is easily understood by considering two simple cases. Let us assume an axially symmetric EFG and choose the direction of $\mathbf{k}_1$ as quantization axis. If we orient the EFG parallel to $\mathbf{k}_1$, the spin precession does not change the projection of I on $\mathbf{k}_1$. As a consequence, the population of the m states with respect to $\mathbf{k}_1$ and thus the correlation function remain constant in time. In case the symmetry axis of the EFG is perpendicular to the direction of the first ($\mathbf{k}_1$) detector, the spin precession causes a periodic oscillation of the projections of I on $\mathbf{k}_1$, corresponding to transitions between the different m states relative to $\mathbf{k}_1$, and a periodic time modulation of the intensity seen by the second detector results, which is invariant under rotation around the symmetry axis of the interaction. Details of the PAC theory can be found in Ref. [18].

For the PAC experiment, we used a commercially available TiO_2 single crystal with the dimensions $(10 \times 10 \times 0.5)$ mm. The crystal was cut with the [001] axis perpendicular to the (10×10) mm faces and the [110] axis perpendicular to the (10×0.5) mm sides. The mother isotope ^{111}In of the ^{111}Cd PAC probe was implanted at room temperature into the (10×10) mm faces with an energy of 160 keV to a dose of $\approx 10^{13}$ ions/cm^2. Following the implantation, the single crystal was annealed at 800 °C for 4 h in order to remove any radiation damage. After this treatment, at least 90% of the probes were found to reside on the regular Ti site.

The time-differential perturbed-angular correlation of the 175 and 247 keV γ-γ transition of the cascade ^{111}Cd was measured with a standard four BaF_2 detectors PAC spectrometer for several orientations of the crystal relative to the detectors. The spectra shown in Figs. 3(a) and 3(b) were obtained with the [001] axis normal to the detector plane. In the case of Fig. 3(a), the [110] axis was parallel to the bisector of two detectors; in Fig. 3(b), it was parallel to one detector. The visual inspection of these spectra already reveals the EFG orientation.

Clearly, the rotation around the [001] direction causes substantial changes of the PAC pattern. This observation immediately discards the [001] direction as the direction of V_{33} because, as pointed out above, in the case of an axially symmetric EFG, the PAC pattern should be invariant under rotation around the symmetry axis of the interaction. In the present case, the EFG presents a slight axial asymmetry

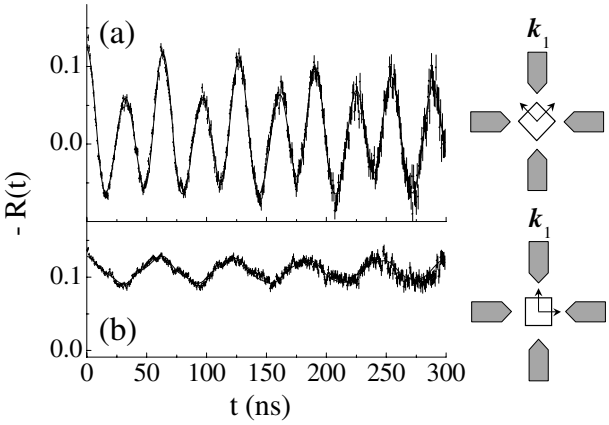

FIG. 3. PAC spectra of the ^{111}In/^{111}Cd-implanted TiO_2 single crystal with (a) the [110] axis pointing at 45° from detectors; (b) the [110] axis pointing to one detector.

($\eta = 0.18$). But even then, the changes upon rotation around the V_{33} axis normal to the detector plane should be imperceptibly small. This is easily checked by calculating the perturbation factor for this geometry.

If in a crystal of tetragonal symmetry such as TiO_2 the EFG is not parallel to the [001] axis, one must expect at least two identical EFG tensors with equal weight but different orientations of the principal axis system. The PAC pattern obtained with the [110] axis at 45° to the detectors [Fig. 3(a)] can be described with a single site, i.e., all ^{111}Cd probes are subject to the same EFG implying that the two expected EFG orientations must be equivalent. With the [110] axis along the bisector of the detectors, two equivalent orientations can be obtained only with V_{33} in the basal plane parallel to either the [110] or the $[1\bar{1}0]$ axis.

A fit of the exact theory [19] to the spectrum of Fig. 3(a) gave the values $\theta \leq 8°$ and $\phi = 43(2)°$ for the angle between V_{33} and the detector plane and the angle between k1 and the projection of V_{33} onto the detector plane, respectively. We estimate that we adjusted the (10×10) mm face of the TiO_2 single crystal parallel to the detector plane within $\pm 5°$. So, the value of $\theta = 0°$ is compatible with the experimental accuracy.

The conclusion of V_{33} lying in the basal plane parallel to either the [110] or the $[1\bar{1}0]$ axis is confirmed by the spectrum in Fig. 3(b). In this case the two EFG orientations are not equivalent. As discussed above, with the EFG parallel to the $\mathbf{k}_1$ detector, the angular correlation remains unperturbed while the EFG normal to $\mathbf{k}_1$ produces a periodic modulation. The superposition of these two configurations leads to a PAC pattern consisting of a small-amplitude oscillation on a constant background. The oscillation is mainly caused by the second configuration, but the exact theory shows that a small oscillatory contribution also comes from the slight asymmetry of the EFG. The least-squares fit to the spectrum in Fig. 3(b) gave the angles $\phi_1 = 3(1)°$ and $\phi_2 = 90(1)°$. The value of the angle θ is consistent with the one obtained from the spectrum in Fig. 3(a). For both spectra the fitted values $\nu_Q = 107.1(3)$ MHz and $\eta = 0.18(1)$ are in good agreement with those previously reported [5,6].

In summary, we have shown that the inclusion of Cd impurities in TiO_2 distorts the oxygen octahedron surrounding the impurity, producing a change in the EFG tensor orientation. Such a change does not result if an isotropic relaxation of the oxygen octahedron is assumed. According to our calculation, the asymmetry of the EFG tensor suggests that Cd in TiO_2 is not neutral, but in a charged state. We therefore conclude that a proper theoretical approach of electronic properties of metal impurities in oxide semiconductors should consider the charge state of the impurity and the impurity-induced relaxations without constraints in a fully self-consistent way.

This work was supported by CONICET, ANPCyT, F. Antorchas (Argentina), and DFG (Germany). M. R. is indebted to J.-P. Dallas (CECM, Vitry) for the single crystals orientation and to A. Traverse (LURE) for valuable support on this project. We thank R. Vianden (ISKP) and A. F. Pasquevich (UNLP) for critical comments.

*Also at LURE, Université Paris-Sud, Orsay, France

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