Anisotropic relaxations introduced by Cd impurities in Rutile TiO$_2$: first-principles calculations and experimental support

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We present an \textit{ab initio} study of the relaxations introduced in TiO$_2$ when a Cd impurity substitutes a Ti atom and the 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 \textit{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 [100] crystal axis.

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 \textit{ab initio} level

Experimental tests of the \textit{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 "shortsighted" 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 test of the \textit{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 \textit{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 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. \textit{Ab initio} calculations 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$_2$.

Recently, the EFG of Cd in TiO$_2$ has been calculated by Sato \textit{et al.} imposing the constraint of isotropic relaxations of the nearest oxygen neighbors and by some of us without this constraint. 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 \textit{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, which has been successfully used to determine the EFG in many compounds. We worked in LDA approximation. We have considered a 2 $\times$ 2 $\times$ 3 supercell of 72 atoms consisting of twelve unit cells of TiO$_2$ (see Fig. 1), where one of the 24 titanium atoms is re-
placed 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 bond. 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 an 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\(_{MAX}\) \([\text{Å}^3]\), 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 8 k-points in the irreducible Brillouin zone for the metallic system (a), and 2 k-points for the non-metallic ones (b). Once self-consistency of the potential was achieved, the forces were computed \([\text{Å}^3]\), the ions were displaced \([\text{Å}^3]\), 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 \([\text{Å}^3]\). We have assumed that relaxations preserve the point-group symmetry of the SC, which restricts O1 and O2 displacements to YZ plane and 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 6 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 \([4, 5]\) and confirms the tendency predicted in the first calculation performed by some of us with a much smaller SC \([6]\). 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 experimental information \([6, 7]\) and are very different from the ones obtained for the neutral state of the impurity, Cd\(^0\). The huge difference obtained in the \(V_{ij}\) 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 \([7]\). The high \(\eta\) 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 I).

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 \(\eta\) 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 \(R_{K_{\text{MAX}}} = 7\), including LO for Cd-4d orbitals, increasing the mesh in \(\vec{k}\)-space, using GGA 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 \(d(\text{Cd-O1})\) and \(d(\text{Cd-O2})\) are converged within 0.01 Å, and \(\eta\) within 0.5 \(10^2\) V/m\(^2\) and 0.1, respectively. Details will be presented in a forthcoming paper \([13]\).

In order to check the change in orientation of \(V_{33}\) from the \(\vec{Z}\) to the \(\vec{Y}\) 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 \(W(\vec{k}_1, \vec{k}_2, t)\) to detect the second \(\gamma\)-ray of a nuclear-decay \(\gamma-\gamma\) cascade at the direction \(\vec{k}_2(\theta_2, \phi_2)\) after a time \(t\) the first \(\gamma\)-ray was detected at the direction \(\vec{k}_1(\theta_1, \phi_1)\), where \(\theta_i\) and \(\phi_i\) describe the propagation direction of \(\gamma_i\) and \(\gamma_2\) 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 \(\gamma_1\)) and thus the angular distribution of \(\gamma_2\). The correlation function \(W(\vec{k}_1, \vec{k}_2, t)\) 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 \(\vec{k}_1\) and \(\vec{k}_2\).

The orientation dependence is easily understood by considering two simple cases. Let us assume an axially symmetric EFG and choose the direction of \(\vec{k}_1\) as quantization axis. If we orient the EFG parallel to \(\vec{k}_1\), the spin precession does not change the projection of \(I\) on \(\vec{k}_1\). As a consequence the population of the \(m\)-states with respect to \(\vec{k}_1\) 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 (\(\vec{k}_1\)) detector, the spin precession causes a periodic oscillation of the projections of \(I\) on \(\vec{k}_1\), corresponding to transitions between the different \(m\)-states relative to \(\vec{k}_1\), 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. \([15]\).

For the PAC experiment, we used a commercially available TiO\(_2\) single crystal with the dimensions 10x10x0.5 mm. The crystal was cut with the [001] axis perpendicular to the 10x10 mm faces and the [110] axis perpendicular to the 10x0.5 mm-sides. The mother isotope \(^{111}\)In of the \(^{111}\)Cd PAC probe was implanted at room temperature into the 10x10 mm faces with an energy of 160 keV to a dose of \(\approx 10^{15}\) 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.

![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.](image_url)
the 175 and 247 keV $\gamma$-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. 3b 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 ($\eta = 0.18$). 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 $\overline{1}0\overline{1}0$-axis.

A fit of the exact theory to the spectrum of Fig. 3(a) gave the values $\theta \leq 8^\circ$ and $\phi = 43(2)^\circ$ for the angle between V$_{33}$ and the detector plane and the angle between $k_1$ and the projection of V$_{33}$ onto the detector plane, respectively. We estimate that we adjusted the 10x10mm face of the TiO$_2$ single crystal parallel to the detector plane within $\pm 5^\circ$. So, the value of $\theta = 0^\circ$ is compatible with the experimental accuracy.

The conclusion of V$_{33}$ lying in the basal plane parallel to either the [110]- or $\overline{1}0\overline{1}0$-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 $k_1$ detector, the angular correlation remains unperturbed while the EFG normal to $k_1$ 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 $\phi_1 = 3(1)^\circ$ and $\phi_2 = 90(1)^\circ$. The value of the angle $\theta$ 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.

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.

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