

Electric-field-gradient calculations for systems with large extended-core-state contributions

P. Blaha

Institut für Technische Elektrochemie, Technische Universität Wien, A-1060 Vienna, Getreidemarkt 9/158, Austria

D. J. Singh

Complex Systems Theory Branch, Naval Research Laboratory, Washington, D.C. 20375-5000

P. I. Sorantin and K. Schwarz

Institut für Technische Elektrochemie, Technische Universität Wien, A-1060 Vienna, Getreidemarkt 9/158, Austria

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Electric-field-gradient (EFG) calculations for TiO_2 in the rutile structure using the standard full-potential linearized-augmented-plane-wave (LAPW) method have shown that the contribution of the Ti $3p$ semicore states is comparable to that of the valence electrons in contrast to other systems studied so far, where the latter dominate. This makes the treatment of the $3p$ and $4p$ states of Ti an important issue. Two-energy-window calculations with different Ti p energy linearization parameters or different sphere radii yield drastically different calculated EFG's. The results of standard LAPW calculations are in poor agreement with experiment. An extension of the LAPW basis with local orbitals, however, yields EFG results close to experiment and removes the sensitivity to sphere radii and energy parameters. The large contribution from the semicore states remains and thus must be considered to be real.

I. INTRODUCTION

Hyperfine interaction measurements can be carried out by various experimental techniques such as by nuclear magnetic resonance (NMR), nuclear quadrupole resonance (NQR), Mössbauer or time-differential perturbed-angular-correlations (TDPAC) spectroscopy. These methods provide an important and valuable tool for experimental investigations of the electronic structure of solids. One of the measured quantities, namely the quadrupole coupling constant $\nu = eQV_{zz}/h$ (where e is the electric charge, h is Planck's constant, and Q is the nuclear quadrupole moment) gives information on the electric-field-gradient (EFG) tensor, whose principal component is V_{zz} . The interpretation of the experimental EFG's in more complicated systems (in particular in systems with d electrons) was often made on the basis of a simple point-charge model.¹ Such an interpretation of EFG measurements could only provide crude information on a possible charge transfer (ionicity), while covalency effects are completely neglected. In fact, the EFG depends sensitively on the electronic charge distribution and in particular on the orbital population.

The EFG can be obtained from the total charge density $\rho(r)$ of the respective system. Since, as mentioned, the EFG is very sensitive to small changes in the charge distribution, especially near the nucleus, an accurate method is needed to determine the crystalline charge density in order to obtain reliable EFG's. Blaha, Schwarz, and Herzig² used the full-potential linearized-augmented-plane-wave (LAPW) method for that purpose, since this method is among one of the most accurate methods available for energy band-structure calculations. Its numerical basis set inside the atomic spheres normally provides a highly precise description of the charge density near the nucleus. First-principles calculations of the EFG's have

been performed² for Li_3N (see below) and then extended to study a series of hcp metals³ showing that this approach yields reliable EFG's, provided that the full potential and good basis sets are used. Recent application to more complicated systems such as the layered TaS_2 compounds⁴ or the high T_c superconductors $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ (Ref. 5) showed that the theoretical EFG usually reproduced the experimental values to within 10–20%. A detailed analysis of contributions to the EFG not only provided information about charge transfer, but also showed that the EFG is very sensitive to the nonspherical charge density around the atom and thus valuable information about chemical bonding, subshell occupations and covalency can be obtained from studying EFG's. One representative example is given for the different oxygen sites in $\text{YBa}_2\text{Cu}_3\text{O}_7$.⁵

In the present paper we will focus on TiO_2 in the rutile structure, for which EFG measurements are available for both atoms.^{6,7} The electronic structure and the charge density of TiO_2 has been investigated using full-potential techniques by Sorantin and Schwarz,^{8,9} who have given a detailed description of the chemical bonding in rutile and related compounds, and by Poumellec, Durham, and Guo,¹⁰ who obtained qualitatively similar band-structure results within the atomic-sphere approximation.

II. EFG CALCULATIONS WITH THE CONVENTIONAL LAPW METHOD

Rutile crystallizes in the tetragonal structure with space group $P4_2/mnm$, where the metal atoms occupy position $2a$ $(0, 0, 0$ and $\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ and the oxygen atoms are at $4f$ $(u, u, 0; 1-u, 1-u, 0; \frac{1}{2}+u, \frac{1}{2}-u, \frac{1}{2}$ and $\frac{1}{2}-u, \frac{1}{2}+u, \frac{1}{2}$ with $u=0.305)$. The Ti atoms are surrounded by a slightly distorted octahedron of oxygen atoms while the latter are threefold coordinated by Ti atoms in the (110)

plane (Fig. 1). The following calculations are extensions of the previous work by Sorantin and Schwarz,^{8,9} who performed band-structure calculations for rutile using the full-potential LAPW method.¹¹ These calculations are performed with a plane-wave cutoff of $R_{MT}K_{\max} = 8$ using 40 special \mathbf{k} points in an irreducible wedge of the Brillouin zone. Further details can be found in Refs. 8 and 9. We emphasize that these are highly converged calculations. Tests with larger basis sets and different Brillouin-zone samplings yielded only very small changes in the results.

The EFG tensor, defined as the second derivative of the Coulomb potential at the atomic positions, can be directly obtained from the total charge density of the crystal.^{2,3} In a multipole expansion of the Coulomb potential only the $L=2$ terms contribute to the EFG, and, for instance, the component V_{zz} can be obtained from the charge density ρ by

$$V_{zz} = \int \rho(r) 2 P_2(\cos\theta) / r^3 dr ,$$

where P_2 is the second-order Legendre polynomial. The resulting tensor is traceless and can be diagonalized yielding the principal EFG component (usually called V_{zz}) and the asymmetry parameter η .

In this paper we will not use the conventional notation in which the coordinate axes are chosen such that $|V_{zz}| > |V_{yy}| > |V_{xx}|$, but use a different local coordinate system for the two positions in order to simplify the interpretation (Fig. 1):

For the Ti site at the corner of the unit cell, the z axis points along the crystallographic c direction, the y axis along $[110]$ (towards the oxygen), and the x axis along the $[\bar{1}10]$ direction. For the oxygen site at $u, u, 0$, the x and c axes coincide, y points along $[\bar{1}10]$, and z points towards the nearest oxygen along the $[110]$ direction.

The first EFG calculations for TiO_2 by Sorantin⁹ showed some unusual results.

(i) There was poor or no agreement with experimental EFG's. For the Ti site, only the V_{zz} component agreed with experiment, but the assignment of the x and y components was interchanged. For the O site the agreement was even worse, since some EFG components were too small by a factor of 2 and the orientation of the tensor was completely different.

(ii) In contrast to all systems studied so far²⁻⁵ (ionic systems, hcp metals, high T_c materials), the EFG at the Ti site was not determined primarily by the valence elec-

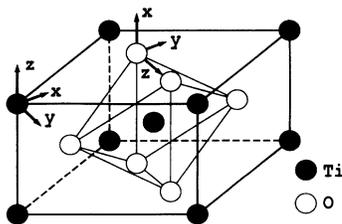


FIG. 1. Unit cell of TiO_2 in the rutile structure and the local coordinate axes used at the two positions.

trons (mainly $4p$ and some $3d$ contributions), but a large contribution came from the semi-core states, i.e., from the Ti $3p$ states which lie approximately -2.4 Ry below the Fermi energy.

In order to obtain a better understanding of the problems arising in this system, we varied the radii of the atomic spheres. In a full-potential calculation, this should not affect the final results, provided that the calculations are well converged, but in TiO_2 we found that a change of the Ti (O) radius from 1.81 (1.81) a.u. to 2.0 (1.6) a.u. modified some EFG components by as much as a factor of 2. Although the O EFG's were changed in the direction of experiment, the agreement remained poor. Further, this sensitivity means that standard two-window LAPW calculations cannot be used to predict the EFG of TiO_2 , since the sphere radii are essentially free parameters in this technique. In order to verify that the sensitivity to linearization parameters (see below) and sphere radii are intrinsic to the standard LAPW method, we (i) carefully checked the convergence with respect to the basis-set cutoff and Brillouin-zone sampling, and (ii) performed parallel calculations using two completely independent codes.¹²

In the LAPW method the reference energy E_l , which is used in the linearization of the energy dependence of the radial wave function $u_l(r, E_l)$, is commonly chosen in the center of the respective (occupied) band.¹¹ In TiO_2 the valence bands consist of low-lying O $2s$ bands followed by bands which mainly originate from the O $2p$ orbitals. The bands which are dominated by the Ti $3d$ character are above the Fermi energy (see Ref. 8 for further discussions). According to this simplified description of the band structure, it is clear that the Ti- p character is only a minor component. Nevertheless, the treatment of the Ti- p states plays a more important role than one might expect in determining the EFG.

When the corresponding reference energy $E_p(\text{Ti})$, at which the Ti p functions are expanded, is chosen between 0.25 and 1.0 Ry (close to E_f at ~ 0.4 Ry), so-called "ghost bands" appear. However, the Ti EFG depends strongly on the choice of this energy parameter, as can be seen from Fig. 2. If $E_p(\text{Ti})$ is chosen below the shaded energy region where the "ghost bands" appear, a Ti $3p$ wave function is formed judged by the number of nodes inside the sphere. In this case V_{zz} is negative and steadily decreases from -1.5 to -4.4×10^{21} V/m² when E_p is raised from -2.1 to $+0.25$ Ry. Above the shaded region, where we have a Ti $4p$ wave function, V_{zz} has the opposite sign and a value of about $+1.4 \times 10^{21}$ V/m². When we compare these results with our final theoretical results, discussed below (see the closed symbols in Fig. 2), the former choice ("3p" wave function) reproduces the "correct" EFG tensor at least in sign (which, unfortunately, could not be determined by experiment), but no quantitative agreement with experiment can be achieved, regardless of the choice of E_p .

As mentioned, these observations lead us to conclude that the standard full-potential LAPW method does not provide reliable EFG's in TiO_2 . This deficiency comes about because Ti has relatively high-lying, so-called "semicore" states (Ti $3p$), which are not "good" core

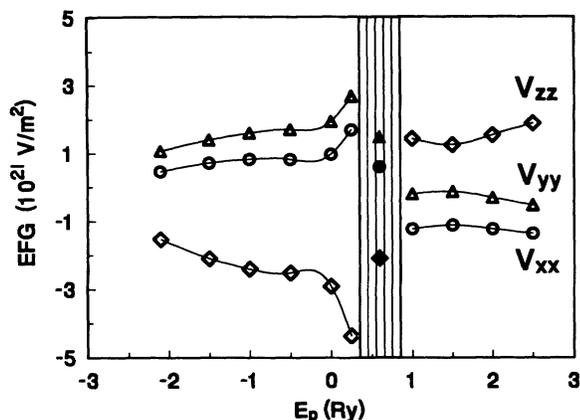


FIG. 2. Ti EFG components (in 10^{21} V/m 2) as a function of the energy parameter E_p (Ti) (in Ry) calculated with the standard full-potential LAPW method (using $R_{\text{Ti}}=2.0$ a.u. and $R_{\text{O}}=1.6$ a.u.). The hatched area indicates the “ghost-band” region, the closed symbols denote the final results using the LAPW+LO method.

states, since they are not confined inside the atomic sphere (approximately 0.45 p electrons lie outside the Ti sphere using a radius of $R_{\text{Ti}}=1.81$ a.u.). Their interactions with neighboring atoms are not negligible, and thus the $3p$ states contribute strongly to the EFG. As a consequence, we must treat these states as band states, and in such a case it is common practice to use a two-window calculation which provides basis functions with either $3p$ or $4p$ character in the two energy regions. Usually this scheme works well, but inherently it suffers from a nonorthogonality problem between the $3p$ and $4p$ states.¹³ With larger Ti spheres (note the sphere-size dependence mentioned above), part of this problem is reduced, but it cannot be removed completely on the basis of the conventional LAPW method. Thus we investigate the possibility of performing predictive EFG calculations by using an approach in which this problem is removed.

III. EFG CALCULATIONS WITH THE LAPW + LO METHOD

In order to calculate reliable EFG’s for TiO $_2$ we have shown that it is necessary to use a method which can accurately treat states with different principal quantum

numbers (e.g., the $3p$ and $4p$ states) while retaining orthogonality. Such a treatment could, for example, be a scheme without linearization, such as the standard APW method, but the latter would require large computational effort when a full-potential treatment is used. Therefore we have chosen a method, recently proposed by Singh,¹³ which provides the required flexibility by including additional basis functions. In this method the standard LAPW basis set is extended with localized orbitals (LAPW+LO). These additional localized orbitals consist of symmetrized linear combinations of two radial wave functions $u_l(r, E_p)$ and $u_l(r, E_p')$ and one energy derivative $\dot{u}_l(r, E_p)$ chosen so that the localized orbital goes to zero with zero derivative at the sphere boundary (with E_p and E_p' near the “semicore” and valence energies, respectively). This basis provides a maximum in flexibility with a minimum of effort [only 4 (9) additional basis functions per atom for sp (d) local orbitals are needed in addition to the standard ~ 100 plane waves per atom of the usual LAPW method]. In a previous application, Singh obtained very good results for the equilibrium properties of fcc La.¹³ This approach has also been applied to calculate the electronic structure of Gd (Ref. 14) and perovskites.¹⁵ The present work is an application to EFG calculations.

Alternate schemes have been implemented by Yu and co-workers¹⁶ and by Singh.¹³ In the first approach, the valence states are explicitly orthogonalized to the semicore states, but the authors report difficulties when they applied it to Y $4p$ and Y $5p$ states in YBa $_2$ Cu $_3$ O $_7$. Singh discussed two alternate approaches called SLAPW-3 and SLAPW-4 by adding radial functions to the LAPW basis set. We note that all these schemes are numerically less efficient (by at least a factor of 2) than the LAPW+LO technique used here.

We have used the LAPW+LO method for the EFG calculations in TiO $_2$ and obtained results drastically different from those of the standard LAPW method. There is no sphere-size dependence of the EFG, and the problem of Ti “ghost bands” does not occur. By comparing our EFG’s with the experimental values^{6,7} (Table I) we find good agreement between theory and experiment for the EFG at both sites. The largest differences occur for oxygen, where V_{xx} is very small, as in experiment, but differs in sign, so that our V_{zz} has a larger magnitude than V_{yy} , in contrast to experiment. Since the EFG is

TABLE I. EFG tensor (in 10^{21} V/m 2) of rutile for the experimental geometry ($u=0.305$). The sign of the EFG components at the Ti site is not known experimentally and is assumed to agree with the present theory (LAPW+LO).

EFG	Ti		O		
	LAPW+LO	expt. ^a	expt. ^b	LAPW+LO	expt. ^a
V_{xx}	+0.60	+0.79	+0.86	-0.17	+0.16
V_{yy}	+1.49	+1.49	+1.34	-1.96	-2.38
V_{zz}	-2.09	-2.28	-2.20	+2.13	+2.22
η	0.43	0.30	0.22	0.84	0.89

^aExperimental EFG values from Gabathuler (Ref. 6).

^bExperimental EFG values from Kanert and Kolem (Ref. 7).

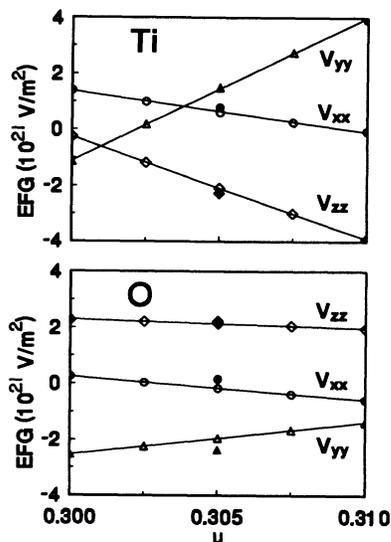


FIG. 3. Dependence of the Ti and O EFG-tensor components (in 10^{21} V/m^2) as a function of the internal u coordinate of the oxygen position ($u, u, 0$). The experimental values are indicated by the closed symbols.

usually very sensitive to structural changes, we have calculated how the EFG tensor depends on the internal coordinate u of the oxygen positions (Fig. 3). We find that all tensor components vary almost linearly with u , but especially the Ti EFG components show a strong dependence. In addition, the total energy is obtained as a function of u (Fig. 4), and minimization leads to an equilibrium value of $u=0.305$, which is the experimental value and close to the minimum obtained by the standard full-potential LAPW method.⁸ At the experimental u , the Ti EFG tensor agrees almost perfectly with experiment. For the oxygen position, the small differences between theory and experiment would disappear for a very slightly different u value of about 0.3025. These results indicate that the EFG, although it is a highly sensitive quantity, can be obtained reliably when the basis is extended to include local orbitals.

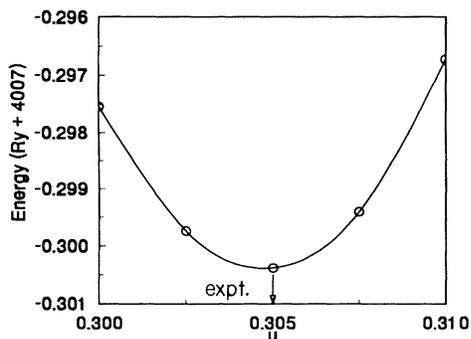


FIG. 4. Total energy (in Ry) as a function of the internal u coordinate of the oxygen position ($u, u, 0$). The experimental u value is indicated by the small arrow.

IV. DISCUSSION AND CONCLUSION

The two methods, the standard LAPW and the LAPW+LO scheme, yield very similar energy bands, densities of states, and structural parameters for TiO_2 . These quantities do not depend strongly on the choice of sphere radii or reference energies E_l . However, the EFG's are highly sensitive to these parameters in a standard LAPW calculation using two energy windows and are in poor agreement with experiment. This high sensitivity of EFG's to the electronic structure amplifies the relatively small errors in the electronic structure using the standard LAPW approach. These errors are greatly reduced with the LAPW+LO extension and the EFG's are obtained unambiguously with this approach. They are found to reproduce closely the experimental values.

A comparison of the two calculations can indicate where the problems in the EFG calculation using the standard LAPW method arise. For the Ti EFG the semicore contributions are large and of similar magnitude in both calculations. The contributions from the O 2s and the valence bands are large as well, but differ significantly between the two methods. This result indicates that the proper orthogonalization of the valence states to the Ti-3p semicore states is essential to obtain a reliable EFG, since the largest errors come from the valence calculation. At the oxygen site, both the semicore and the O-2s states yield small contributions to the EFG, so that the valence states determine the EFG. The treatment of the Ti- p states in the valence region has a significant effect on the EFG at the O site. This can be understood, since, as mentioned, the most significant errors are in the valence bands, which are hybridized.

Basically, the EFG at the Ti site can be explained as partial cancellation between the "on-site" semicore and the "off-site" Ti $4p$ contribution. The "on-site" Ti $3p$ states are polarized by oxygen such that a small redistribution of charge occurs, where those p states pointing towards oxygen are depleted. The "off-site" Ti $4p$ contributions correspond to the (orthogonalized) tails of the O 2s and $2p$ wave functions reaching into the Ti sphere, where they are expanded in partial waves. Thus a larger p charge is found in orbitals pointing towards the oxygen atoms, and therefore this "off-site" contribution has a sign opposite to that of the "on-site" part.

Rutile is thus shown to be a compound in which the semicore states have a giant contribution to the EFG. In most systems studied so far, they contribute a few percent at most. In TiO_2 we have shown that the proper treatment of the states with different principal quantum numbers (such as the Ti $3p$ and $4p$ in TiO_2) is essential and can be efficiently done using the LAPW+LO method.

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