First-principles study of the nuclear quadrupole resonance parameters and orbital ordering in $LaTiO_3$

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The electronic structure of the distorted perovskite $LaTiO_3$ is studied using density-functional theory, implemented with a projector-augmented wave formalism together with the local-density approximation plus Hubbard U-parameter (LDA+U) model. Various experimentally determined quantities, including the antiferromagnetic ordering and spin moments and electric field gradients at the lanthanum and titanium sites, are well reproduced. It is found that the excess spin density on the titanium sites, which accounts for the antiferromagnetism, is very well described by the conjectured $d_{xy}+d_{yz}+d_{zx}$ orbital configuration.

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I. INTRODUCTION

The distorted perovskite $LaTiO_3$ is an insulator with antiferromagnetic order.[1] In an idealized undistorted structure, the Ti^{+3} sites would have electronic configuration t_{2g}^1, and hence a simple band model would predict this compound to be metallic. In fact, $LaTiO_3$ undergoes a Jahn-Teller distortion, and additionally there are strong electron correlation effects at the titanium sites. The result is an insulating antiferromagnetic ground state with an ordered moment of $0.57\mu_B$. If the distortion fully quenched the orbital angular momentum of the titanium $3d$ shell, an ordered moment of $1\mu_B$ would result; the smaller value suggests an interesting interplay between the spin and orbital degrees of freedom in this compound. Cwik *et al.*[1] on the basis of careful crystallographic work conjectured that the orbitally ordered state is, in fact, $\frac{1}{\sqrt{3}}(d_{xy}+d_{yz}+d_{xz})$, and subsequently Kiyama and Itoh[2] argued that the experimental nuclear magnetic resonance (NMR) and nuclear quadrupole resonance (NQR) spectra supported this proposal. Computational work by Okatov *et al.*[3] revealed an orbitally ordered ground state in accord with this conjecture, but the nuclear-magnetic-resonance (NMR) parameters were not addressed in that study. Because the interpretation of the NMR parameters to date has depended in part on point-charge models,[2,4] which are in general not very accurate, we undertook to investigate the ground state, magnetic resonance, and orbital ordering in this compound using a detailed first-principles approach. Thus the purpose of this contribution is to investigate the electronic ground state and the assignment of the magnetic-resonance spectra in $LaTiO_3$; we use the excellent agreement found between the computed and measured magnetic-resonance parameters as validation of the theoretical model used. We then compared the resulting spin densities to the state conjectured by Cwik *et al.*[1] and find that it is confirmed in quantitative detail. In addition, we propose that an increase in electric field gradient at a metal site in a transition-metal oxide is evidence for significant (compared to the local-density approximation) electron correlation effects and explain the increase as arising from the enhanced coupling of d-band electrons to the electric field gradient tensor operator as compared to other orbital symmetries.

II. METHODS

The present results have been obtained using the ABINIT code,[5,6] a density-functional theory code implemented with pseudopotentials and plane waves. It is a common project of the Université Catholique de Louvain, Corning, Inc., and other contributors.[7] The projector-augmented wave (PAW) method was used,[8–10] using data generated by the ATOMPAW code[11] modified for use with ABINIT. Relevant atomic parameters are listed in Table I. In this method, all-electron accuracy for the valence space is recovered from a pseudopotential calculation using a projection method. For many of the observables studied here, most notably the electric field gradient at the atomic positions, other plane-wave-based methods do not give sufficient accuracy.

The electronic structure was computed with the local-density approximation plus Hubbard U-parameter (LDA+U) model.[12] In previous work on $LaTiO_3$, a range of U values was investigated for the titanium $3d$ orbitals, and the best results were found with U in the 3–4 eV range.[3] There it was also observed that the correct band ordering was obtained only when a U of 8 eV was applied to the lanthanum $4f$ orbitals. In the present study we also examined a range of U values on titanium $3d$ and two values (0 and 8 eV) on lanthanum $4f$. All calculations were performed using two spin densities, and trials were made using two independent spin polarizations (allowing for any type of scalar magnetization) or just one (forcing antiferromagnetic ordering). The unconstrained calculations converged to the antiferromagnetic state but are computationally more expensive, so pro-

TABLE I. Atomic parameters used in the present study. For each atom, the valence electron configuration is given, followed by the total number of PAW projectors and their angular momenta, the PAW radius in atomic units (all projectors were constructed using the same radius), and the nuclear quadrupole moment in barns used in the electric field gradient calculations.

Atom	Valence	Projected	Radius	q_{zz}/bn
La	$5s^25p^66s^25d^1$	$2s$, $2p$, $2d$, $1f$	3.0	0.22
Ti	$3s^23p^64s^24p^63d^2$	$2s$, $2p$, $2d$	2.3	0.24
O	$2s^22p^4$	$2s$, $2p$	1.41	−0.0261

duction runs were made using the antiferromagnetic constraint. A plane-wave energy cutoff of 25 hartree was used together with a cutoff on the PAW fine grid of 50 hartree. A $6\times6\times4$ shifted Monkhorst-Pack grid was used to sample reciprocal space, which for the $LaTiO_3$ unit cell leads to a grid spacing of about 0.03 $Å^{-1}$. In these calculations, the net spin densities at different atomic sites could be extracted and these data were used to estimate the magnetic moment and ordering.

In order to compare to experimental data on the electronic structure, specifically nuclear magnetic and nuclear quadrupole resonance, the electric field gradient (EFG) tensor at each atomic site was computed using the total electronic density and the PAW all-electron reconstructions.[13,14] We recently implemented this approach into ABINIT,[13] based on the work of Profeta *et al.*,[14] in a way that allows for metallic occupancies and hence is suitable for materials that are or could be metallic and/or magnetic, as is the case here. In the nuclear magnetic and nuclear quadrupole resonance experiments,[2,4] the parameter extracted from the spectra is the quadrupole resonance frequency ν_Q, defined in terms of the EFG by

$$\nu_Q = \frac{3eQV_{zz}}{2hI(2I-1)}, \tag{1}$$

where V_{zz} is the largest principal component of the EFG at the nuclear site, eQ is the electric-quadrupole moment of the nucleus, I is its spin, and h is Planck's constant. For comparison with experiment we converted our calculated values of the EFGs to quadrupole frequencies using the same values for the electric quadrupole moments as used in the experimental work.[2,4]

A second parameter is needed to characterize fully the EFG tensor (it is a traceless rank-two tensor and so requires just two parameters) and that is conventionally the asymmetry. For principal tensor components ordered in magnitude from largest (V_{zz}) to smallest (V_{xx}), the asymmetry is defined as

$$\eta = \frac{V_{xx} - V_{yy}}{V_{zz}}. \tag{2}$$

III. RESULT AND DISCUSSION

Table II collects results of various parameters computed by the methods outlined above and compares them to experiment. As noted, a range of U parameters was investigated, and we found that the best agreement of the NMR parameters with experiment occurred for a titanium U in the 3–4 eV range and lanthanum U of 8 eV, as was found for other properties in earlier work.[3] The table shows first that the calculated value of the ordered moment in the insulating antiferromagnetic state, using the LDA+U approximation, is quite close to that determined experimentally by Cwik *et al.*[1] Of course, within the simple LDA, a nonmagnetic metal is found, as expected, because this approximation fails to account for the strong electron correlation at the metal sites. Second, the lanthanum-139 EFG results are in good agreement with experiment[4] in both LDA and LDA+U. Because lanthanum is present here as La^{3+}, it has donated its electron density to the other species and acts primarily as an inert cation. This inertness is reflected in the fact that its local EFG is relatively insensitive to the various approximations being applied to the titanium sites. The titanium magnetic-resonance response, however, is strongly affected by the level of electron correlation approximation used. In the simple LDA model, agreement between ν_Q in theory and experiment is poor but is dramatically improved in LDA+U.

TABLE II. Observables computed with various first-principles models together with experimental results from the literature. In the column labeled LDA+U, Hubbard U parameters of 3 eV on titanium $3d$ orbitals and 8 eV on lanthanum $4f$ orbitals were used.

Observable	LDA	LDA+U	Expt.
Magnetic moment/μ_B	0.0	0.52	0.57[a]
La-139 ν_Q/MHz	3.663	3.691	3.8[b]
La-139 η	0.594	0.592	0.6[b]
Ti-49 ν_Q/MHz	0.792	1.46	1.6,[c] 2.3[b]
Ti-49 η	0.419	0.568	0.35[b]

[a]Reference 1.
[b]Reference 4.
[c]Reference 2.

It has been observed in other studies also[15] that in strongly correlated electron systems, where the LDA+U method provides an accurate description as compared to LDA itself, the EFG is typically underestimated substantially by LDA alone. However, in LDA+U, the computed EFG increases significantly and typically agrees well with experiment. The dependence of the EFG, as measured by ν_Q, in $LaTiO_3$ is shown in Fig. 1. This figure shows that the EFG increases markedly with the on-site correlation for titanium, although interestingly the lanthanum EFG is largely insensitive to the lanthanum U value (Table II). We would suggest that a large increase in EFG at a given metal site in a metal

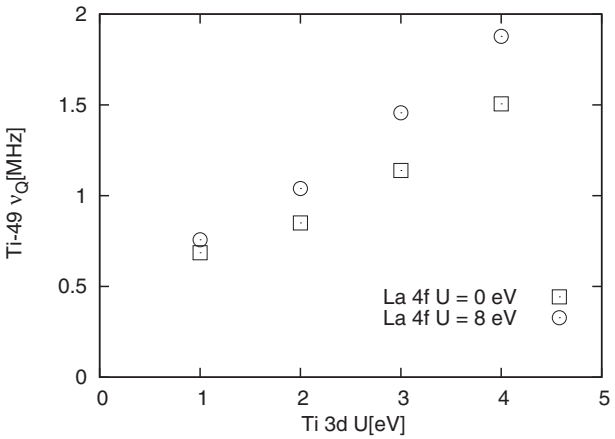

FIG. 1. Dependence of the ^{49}Ti quadrupole resonance frequency ν_Q on the value of Hubbard U parameter applied to the titanium $3d$ orbitals. Results with a U value on the lanthanum $4f$ orbitals of 0 and of 8 eV are shown.

oxide is evidence for significant electron correlation effects at that site, although the lanthanum case indicates that the converse need not be true. The difficulty with this proposal of course is in identifying a suitable reference by which to judge the increase. In the work of Kiyama and Itoh,[2] it is argued that the increase in EFG at the titanium site in $LaTiO_3$ as compared to Ti^{4+} compounds such as $MgTiO_3$ cannot be explained solely by strain around the titanium site but indicates an increased departure of the *d* orbitals from a spherical charge distribution. The present calculations provide some hint as to the origin of this departure because they show that the electron density at the Ti site is about the same in both LDA and LDA+*U*, although ν_Q is substantially increased in the latter case (Table II). In the LDA+*U* calculation, the extra on-site electron correlation added to the *d* orbitals of titanium stabilizes a *d* band, leading not to a total increase in Ti electron density but rather to a rearrangement of density from (in this case) *s*, *p*, and *d* channels to an excess in the *d* channel. Now, because the EFG interaction transforms like a pure rank-2 spherical tensor, it is constructed from Gaunt integrals such as $\langle Y_{lm}|Y_{2m}|Y_{l'm'}\rangle$, and so redistribution of electron density from *s* and *p* channels (which couple poorly or not at all by this mechanism) to *d* channels (which couple efficiently) leads to a significantly increased EFG. The lanthanum EFGs are not so affected because the Hubbard *U* parameter was applied to the 4*f* orbitals, and so any enhanced population does not lead to stronger coupling into the EFG.

Concerning the orientation of the Ti EFG tensor with respect to the crystal axes, our results show that the principal component is aligned roughly midway between the crystal *b* and *c* axes, not along the *b* axis as a point-charge model had suggested.[4] Many of the conclusions drawn from the earlier NMR work[2,4] remain valid despite this difference because the relative orientation of the EFG tensor and other coupling tensors in NMR spectra typically make only a small difference in the resulting spectrum. Nonetheless, we point it out here because particularly in materials with interesting and complex electronic structure, it is to be expected that the point-charge model will give poor results.

We turn now to the orbital ordering. Our calculations provide the density matrices for the correlated orbitals for each spin component. To focus on the contribution to the antiferromagnetic order, we investigated the difference in spin components at each site. When converted to the same coordinate system as used by Cwik *et al.*,[1] we find *d*-orbital populations of $0.118d_{xy}$, $0.115d_{yz}$, and $0.118d_{xz}$, with ≤ 0.01 in d_{z^2} and $d_{x^2-y^2}$. The essentially equal values for these components are to be compared to the conjectured orbitally ordered state, $\frac{1}{\sqrt{3}}(d_{xy}+d_{xz}+d_{yz})$, which suggests the same equality of populations. The spin component difference is plotted from the computed electron density in Fig. 2, where the same orbital shapes as conjectured by Cwik *et al.*[1] may be observed.

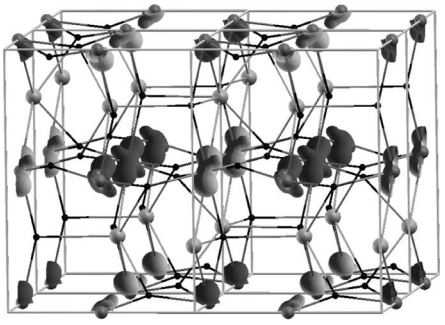

FIG. 2. Net spin density in $LaTiO_3$ using LDA+*U*. Here the oxygen atoms are the small spheres, lanthanum atoms are the larger spheres, and the complex shapes are the net spin densities, which all are located on the titanium sites. The antiferromagnetic order is shown by their alternating shading, while the orbital order is detected by their alternating alignment. The experimentally determined spin moment is well reproduced, as are the measured NQR parameters La and Ti (Table II). The conjectured orbitally ordered state matches the spin density pictured here, both qualitatively and quantitatively.

IV. CONCLUSIONS

In this contribution we have used density-functional theory in the projector-augmented wave implementation together with the LDA+*U* approximation to study the electronic ground state of the distorted perovskite $LaTiO_3$. We computed the NMR observables at both the lanthanum and titanium sites and found good agreement with experiment and also found an ordered antiferromagnetic moment in agreement with experiment. Having thus validated our electronic model, we compared the net spin densities at the titanium sites to the model for orbital ordering in this system and found quantitative agreement. Finally, on the basis of the observed increase in EFG in strongly correlated transition-metal oxides as compared to oxides with more conventional electronic structure, we proposed that such an increase in EFG is evidence for strong electron correlations at the metal sites. The mechanism for such an increase is the stabilization of a *d* band and the concomitant redistribution of electron density from *s* and *p* orbitals to *d* orbitals. This effect increases the EFG because the symmetry of the EFG tensor (pure rank 2) matches the *d*-orbital symmetry and hence such orbitals couple more efficiently than others, leading to enhanced EFGs.

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