Investigation of the Jahn-Teller Transition in TiF₃ using Density Functional Theory.

Vasili Perebeinos and Tom Vogt
Department of Physics, Brookhaven National Laboratory, Upton, New York 1973-5000
(Dated: September 18, 2018)

We use first principles density functional theory to calculate electronic and magnetic properties of TiF₃ using the full potential linearized augmented plane wave method. The LDA approximation predicts a fully saturated ferromagnetic metal and finds degenerate energy minima for high and low symmetry structures. The experimentally observed Jahn-Teller phase transition at T_c≈370K cannot be driven by the electron-phonon interaction alone, which is usually described accurately by LDA. Electron correlations beyond LDA are essential to lift the degeneracy of the singly occupied Ti t₂g orbital. Although the on-site Coulomb correlations are important, the direction of the t₂g-level splitting is determined by the dipole-dipole interactions. The LDA+U functional predicts an antiferromagnetic insulator with an orbitally ordered ground state. The input parameters U=8.1 eV and J=0.9 eV for the Ti 3d orbital were found by varying the total charge on the TiF₆⁻ ion using the molecular NRLMOL code. We estimate the Heisenberg exchange constant for spin-1/2 on a cubic lattice to be approximately 24 K. The symmetry lowering energy in LDA+U is about 900 K per TiF₃ formula unit.

PACS numbers: 71.15.Mb,71.15.-m,71.30.+h,64.60.-i

I. INTRODUCTION

There is an ongoing interest in phase transitions in perovskite based materials. Above T_c≈370 K the trifluoride TiF₃ has the cubic framework perovskite structure AMX₃, with no A cations present. Each Ti is at the center of a corner sharing fluorine octahedra MX₆. At low temperatures the structure becomes rhombohedral. This symmetry lowering can to a first approximation be characterized by a tilting of the rigid MX₆ octahedra about the threefold axis. The nominal valance of the titanium ion is 3+, with one 3d electron occupying the triply degenerate t₂g orbital in the high temperature phase. One may expect a Jahn-Teller instability in TiF₃. Indeed in the distorted structure titanium has a D₃d local environment, in which the t₂g orbitals are split into an a₁g and a doublet e₂g orbital. The trigonal distortions have been intensively discussed in the context of other t₂g compounds, like FeO [1] and LaTiO₃ [2].

We use Density Functional Theory (DFT) to investigate the cubic to rhombohedral structural phase transition which has been established by X-ray diffraction [3,4]. Many trifluoride MF₃ compounds (M=Al, Cr, Fe, Ga, In, Ti, V) exhibit this structural phase transition [3,5,6,7]. It is believed that the observed transition in TiF₃ is of a ferroelastic nature [3]. In most of those materials except for TiF₃ and MnF₃ there are no partly filled d shells. The driving mechanism for the ferroelastic transitions can be pictured as the formation of the dipole moments on fluorine atoms due to the asymmetric distribution of the 2p electron density in the distorted structure. The long range dipole-dipole interaction favors a distorted structure with anti-polar arrangement of dipoles [3]. The Local Density Approximation (LDA) captures both the long-range and the short interactions on the same footing and predicts a distorted structure to have a minimum energy in AlF₃ [5].

In the present studies we choose the TiF₃ system with a partly filed t₂g shell. The Jahn-Teller energy lowering due to the lifting of the t₂g orbital degeneracy in the distorted structure should add up to the long range dipole formation energy. Unexpectedly, we find the total energies of the high and low temperature phases to be identical within the errors of calculations. The failure of LDA to explain this phase transition is due to the fact that transition metal d electrons are not adequately described by LDA. Although the dipole-dipole long range interaction favors the distorted structure, however the electron kinetic energy of the t₂g one third filled band is increased due the diminishing of the hopping integral (t) between the neighboring Ti atoms due to the octahedra tilting. The two effects mutually cancel each other resulting in degenerate minimums of the potential energy surface.

It was realized some time ago that LDA tends to underestimate the Coulomb repulsion of electrons occupying different orbitals of the same d-shell [8]. In particular, this leads to equal occupations of different orbitals of the same manifold and prevents the stabilization of the orbitally ordered solutions. The LDA+U functional, however, generates an orbital dependent potential which favors solutions with broken orbital degeneracy. LDA+U calculations indicate that the low temperature phase has a by about 900K lower energy per TiF₃ than the high temperature phase. One of the roles of the Coulomb interaction is to suppresses the electron kinetic energy of the partly filled t₂g bands. The bandwidth narrowing in the distorted structure effectively reduces the restoring force to rotate the octahedra which facilitate stabilization of the distorted structure. The electronic ground state is orbitally ordered in the low temperature phase with one electron occupying the a₁g orbital oriented along the rhombohedral direction forming a Heisenberg spin 1/2 lattice coupled antiferromagnetically to its neighbors via a superexchange mechanism.
In this work we use the molecular NRLMOL code \cite{10} to calculate $U$ by varying the occupation number of the Ti $d$ orbital of the TiF$_6^{2-}$ ion. These calculations are significantly less computationally demanding compared to the supercell approaches \cite{3, 11, 12} and since only the first neighboring fluorines mostly contribute to the screening a good estimate for parameters $U$ and $J$ can be readily achieved in the calculations.

The Hund interaction and the electron kinetic energy are realistically described with LDA. The TiF$_3$ compound is predicted to be a ferromagnetic metal with a fully saturated magnetic moment of 1 $\mu_B$ per formula unit. The exchange Hund energy is large and the Stoner criterion is satisfied. The electron-phonon interaction lifts the on site degeneracy of the $t_{2g}$ orbitals and for a sufficiently strong coupling a gap in the spectrum can open. We estimate the electron-phonon coupling ($\approx 2$ meV/degree) to be insignificant to open the gap and to drive the phase transition in TiF$_4$. Although the on-site Coulomb correlations are important, the direction of the $t_{2g}$-level splitting is determined by the long range dipole-dipole interaction \cite{5}. Many successes and failures of LSDA in transition metal oxide compounds have been summarized, for example, in the review article \cite{13}.

II. METHOD OF CALCULATION

The purpose of this paper is to elucidate the electronic structure of TiF$_3$ and explain the structural phase transition using the DFT method. This is done using the full potential linearized augmented plane wave (FP-LAPW) method \cite{14} with local orbital extensions \cite{15} in the WIEN2k implementation \cite{16}. The LDA Perdew Wang \cite{17} exchange-correlation potential was used. Well converged basis sets and Brillouin zone sampling were employed. The crystal structure was reported by Kennedy and Vogt \cite{4}. It is cubic at high temperature with a unit cell volume 58.8 (Å$^3$). A rhombohedrally distorted structure of the space group R-3c can be characterized by three parameters: (1) volume 56.5 (Å$^3$), (2) the octahedra tilt $\phi = 13^\circ$, and (3) a $c/a = 1.0315$ ratio, which measures the distortion along the rhombohedral direction. There are two titanium and 6 fluorine atoms in the rhombohedral unit cell. The fluorine ions are sitting in the 6e sites ($x, -x + 1/2, 1/4$, etc.), and $\delta = x - 0.75$ is the deviation from cubic positions. The octahedra tilting angle is related to $\delta$ by $\tan(\phi) = 2\sqrt{2}\delta$. The calculations for both the high and low symmetry phases were performed using two formula per unit cell and the same k-point mesh, with 292 special k-points in the irreducible Brillouin zone. A tetrahedron method was used for integration over the Brillouin zone.

III. LDA RESULTS

We first calculate the cubic phase by fixing $\phi = 0$ and $c/a = 1$ in the rhombohedral structure of the space group R-3c. LDA finds a ferromagnetic ground state solution with a fully saturated magnetic moment of 1 $\mu_B$ per Ti. The volume optimization is shown in Fig. 1. The equilibrium volume $V_0 = 58.6$ Å$^3$ is in excellent agreement with the experiment \cite{4}. The bulk modulus of 111 GPa is extracted by fitting a Murnaghan \cite{18} equation of state. The $c/a$ ratio was fixed to the experimental value 1.0315 at T=10 K and the two parameters are relaxed to find the minimum of the low symmetry structure. The energy minimization with respect to the volume for the fixed $c/a=1.0315$ and $\phi = 10^\circ$ is shown on Fig. 1 and yields $V_n = 56.2$ Å$^3$.

Further optimization with respect to the tilt angle for a fixed minimum volume $V_n$ and the same $c/a$ ratio did not significantly alter the ground state energy. The optimal tilt angle is $\phi_0 = 10.5^\circ$. The Ti-F bond is the most rigid bond in the structure, and therefore it is convenient to plot the energy versus the Ti-F bondlength. A parabola fit to the energy variation shown on Fig. 2 is excellent and yields a spring constant of the single bond $K = 13.9$ eV/Å. The Ti-F bond length $d$ in R3c crystal structure is

$$d^2 = a_h^2(1/12 + \delta^2 + (c/a)^2/24)$$  \hspace{1cm} (1)

where $a_h = a\sqrt{2}$ is the hexagonal a lattice constant. Knowing the spring constant for the bond stretching and equilibrium volume $V_0$ the bulk modules can be estimated as $B = K/(6V_{0}^{1/3}) \approx 96$ GPa.

The total energy differences of the high- and low-T phases is beyond the accuracy of calculations. Despite the excellent agreement with the experimental structural
parameters, the LDA total energy analysis does not explain the high temperature of the observed structural phase transition.

The densities of states are shown on Fig. 3. The \( t_{2g} \) band lies at the Fermi level and it is one third filled. The Hund energy dominates the kinetic energy such that the Stoner criterion is satisfied and the material becomes magnetic. The band structure of the Ti \( t_{2g} \) electrons can easily be understood with a nearest-neighbor two-center Slater-Koster [20] model. The orbitals \( |\alpha\beta\rangle \) have hopping matrix elements with themselves along the \( \alpha \) and \( \beta \) directions with amplitude \( t=(dd\pi) \). The tight binding fit in the high temperature phase with \( t = 0.25 \) eV is shown on Fig. 4.

In the low temperature phase the Ti-F-Ti bond angle is smaller than 180°, which reduces the hopping and narrows the band width. The onsite orbital degeneracy is lifted by the octahedra tilting. In the \( D_{3d} \) local Ti site symmetry the \( t_{2g} \) manifold splits into:

\[
\begin{align*}
a_g &= \frac{|xy|+|yz|+|zx|}{\sqrt{3}} \\
e_{g1} &= \frac{|yz|-|zx|}{\sqrt{2}} \\
e_{g2} &= \frac{2|xy|-|yz|-|zx|}{\sqrt{6}}
\end{align*}
\]  
(2)

The bandwidth in the tilted structure \( \phi = \phi_0 \) corresponds to reduced \( t=0.225 \) eV and the electron-phonon Jahn-Teller energy gap at \( \Gamma \) point is 6 meV. From the simple tight binding model with these parameters the kinetic energy loss due to the band narrowing effect is 18 meV and it is not even compensated by the lifting of the orbital degeneracy. The total LDA energy includes the lattice and electronic degrees of freedom and predicts degenerate minima within the errors of calculations (Fig. 1). The LDA failure to predict the cubic-to-rhombohedral phase transition can be rationalized by the lack of electron correlation effects in the LDA method.

IV. Parameter \( U (J) \) Calculation for LDA+U Method

In extending the LDA method to account for correlations resulting from on-site interactions Anisimov, Zaanen, and Andersen (AZA) [9] chose to refine LDA by including an orbital-dependent one-electron potential to
account explicitly for the important Coulomb repulsions not treated adequately in the LDA approach. This was accomplished in accordance with Hartree-Fock theory by correcting the mean-field contribution of the \(d-d\) on-site interaction with an intra-atomic correction. This correction has been applied in slightly different ways. We use the SIC LDA+U functional \(^1\) as implemented in the WIEN2k package.

In this work we use a single TiF\(_6^{2-}\) ion to calculate parameters \(U\) and \(J\). In these calculations the screening due to the nearest neighboring fluorines is taken into account and there are no other Ti atoms for the \(d\) electron to hop to. The TiF\(_6^{2-}\) ion forms an octahedra with a Ti-F bond of 1.93 \(\text{Å}\) with the Ti atom placed in the center. The total energy and \(d\) orbital chemical potential of the TiF\(_6\) can be modelled by the single site Hubbard model:

\[
E = E_0 - \varepsilon(n_\uparrow + n_\downarrow) + \frac{U}{2} (n_\uparrow + n_\downarrow)^2 - \frac{J}{2} (n_\uparrow^2 + n_\downarrow^2) \\
\mu_\uparrow = \frac{\partial E}{\partial n_\uparrow} = -\varepsilon + U(n_\uparrow + n_\downarrow) - Jn_\uparrow
\]

where \(n_\uparrow\) and \(n_\downarrow\) are occupation numbers of the triply degenerate \(t_{2g}\) molecular orbital. We use two sets of self-consistent calculations to determine the parameters \(U\) and \(J\). The quadratic total energy and linear chemical potential fits to the nonmagnetic calculations give \(U_{t\uparrow}^{eff} = U - J/2 = 7.66\) eV. From the fully polarized magnetic calculation the quadratic energy and linear \(\mu_{1/2}\) fit we find \(U_{t\uparrow}^{eff} = U - J = 7.24\) eV, such that \(U = 8.08\) eV and \(J = 0.84\) eV. The Hund coupling parameter \(J\) should be compared with the spin up and down energy bands splitting in ferromagnetic LDA calculations Fig. \(6\) which is \(J = 0.87\) eV.

V. LDA+U RESULTS

The volume optimization of the high symmetry phase gives \(V_0 = 61.8\) \(\text{Å}^3\) using two formula per unit cell with \(R-3c\) point group symmetry operations and fixed \(\phi = 0^\circ\) and \(c/a = 1\). The bulk modulus extracted from the Murnaghan fit shown on Fig. \(5\) is 110 GPa. The electron correlations on the Ti \(d\) orbitals reduces the bandwidth \((4t/U)\), such that the kinetic energy variation with respect to the lattice constant is smaller in the LDA+U functional resulting in a larger equilibrium lattice constant compared to the LDA result.

The low symmetry optimization was first done with respect to volume for a fixed experimental tilt angle \(\phi = 12^\circ\) and the ratio \(c/a = 1.0316\). The optimal volume is 58.1 \(\text{Å}^3\). Further optimization with respect to the tilt angle for the fixed equilibrium volume gives an additional energy gain of 130 K per Ti such that the distorted structure with the optimal tilt angle of 14\(^0\) is lower in energy by 675 K per Ti. The parabola fit to the Ti-F bond length variation shown on Fig. \(6\) gives spring constant \(K = 15.95\) eV/\(\text{Å}^2\). The corresponding bulk modulus \(B = K/(6V^{1/3})\) \(\approx 108\) GPa is an in excellent agreement with Murnaghan fit Fig. \(5\).

The density of states for the distorted structure is shown on Fig. \(6\). The fluorine \(2p\) states are not much affected by the correlations. Whereas dramatic differences are seen for the Ti \(d\) states. First, LDA+U predicts a gap for both high-T and low-T phases in the \(t_{2g}\) band, which is split into three distinct narrow peaks originated from the \(e_g\) and two \(e_g\) orbitals. The imposed rhombohedral symmetry of the supercell makes the lowest energy states...
The Hubbard Hamiltonian:

\[ \mathcal{H}_{el} = \sum_{i,\alpha\beta,\sigma} -t \left( c_{i\alpha\beta,\sigma}^{\dagger} c_{i+\alpha,\sigma} + c_{i+\alpha,\sigma}^{\dagger} c_{i\alpha\beta,\sigma} \right) + \sum_{i,\alpha\beta,\sigma} U/2 (n_{i\alpha\beta,\sigma} n_{i\alpha\beta,\sigma} - n_{i\alpha\beta,\sigma} n_{i\alpha\beta,\sigma}) + \sum_{i,\alpha\beta\neq\alpha'\beta',\sigma,\sigma'} U' - J \delta_{\sigma,\sigma'} (n_{i\alpha\beta,\sigma} n_{i\alpha'\beta',\sigma'} - n_{i\alpha\beta,\sigma} n_{i\alpha'\beta',\sigma}) \]  

(4)

The superexchange energies per Ti of the antiferromagnetic Neel state and ferromagnetic solutions, with \( a_g \) orbital Eq. 2 occupied in both cases, are:

\[ E_{AFM} = \frac{4t^2}{3} \frac{1}{U'} - \frac{8t^2}{3} \frac{1}{U} \]

\[ E_{FM} = \frac{4t^2}{3} \frac{1}{U'} - \frac{1}{U'} - J \]  

(5)

where the first term is due to virtual hopping of the localized electron on the six neighboring \( e_g \) orbitals. The second term in \( E_{AFM} \) is due to virtual hopping of the \( a_g \) orbital to the 6 neighbors with the hopping amplitude \( 2t/3 \), and it is missing in the ferromagnetic ground state due to the Pauli principle. The \( LDA + U \) energy differences between the ferromagnetic and antiferromagnetic ground states and the fixed optimal distorted geometry are shown on Fig. 8. Both the perturbation theory and the \( LDA + U \) results predict the antiferromagnetic to ferromagnetic transition at \( U/J \approx 4 \). For the large \( U/J \) values \( LDA + U \) underestimates the exchange energy by a factor of 2 and for the realistic parameter of \( U = 8.1 \) eV it predicts an energy difference of 72 K between the two phases. Neglecting the zero-point energy of the spin waves the energy difference between the parallel and antiparallel classical spins on a cubic lattice is \( 6JS(S+1) \). For spin \( S = 1/2 \) this yields \( J = 16 \) K and the corresponding Neel temperature in the mean field approximation is \( T_N = 1.5J = 24 \) K. The quantum fluctuations reduce the Neel temperature to \( T_N = 0.946J = 15 \) K. However, the neutron diffraction experiment did not reveal any long range magnetic order down to 10 K. Whether the absence of magnetic long range order in TiF\(_3\) is an intrinsic effect due to the coupling of the orbital and spin degrees of freedom or extrinsic due to the presence of the multidomain structure observed in the low symmetry phase by Mogus-Milankovic et al. requires further theoretical and experimental investigations.

VI. PRESSURE ANOMALY

X-ray diffraction measurements under pressure by Sowa and Ahsbahs allow us to determine the experimental bulk modulus of TiF\(_3\). Fig. 9(a) shows data points along with Birch-Murnaghan equation of state fit. The fit to the full range of pressures predicts a physically unreasonable small bulk modulus \( B = 7.5 \) GPa and unphysically large coefficient \( K_2 = 142 \) GPa\(^{-1}\). The first derivative is fixed to \( K_1 = 4 \) in the Birch-Murnaghan equation of state:

\[ P(V) = 3Bf(1 + 2f)^{5/2} \left( 1 + \frac{3f^2}{2} \left( BK_2 + \frac{35}{9} \right) \right) \]  

(6)
where \( f = 0.5((V_0/V)^{2/3} - 1) \) and \( V_0 \) is the volume at ambient pressure. The high pressure points (above 4 GPa) can be fitted by Eq. 6 to give \( B = 51 \) GPa and a normal \( K_2 = -0.005 \text{ GPa}^{-1} \). However, the volume at normal pressure has to be fixed to \( V_0 = 51.9 \text{ Å}^3 \), which is 11% smaller than the observed one.

In the present work we calculate the bulk modulus of the lower symmetry phase using the experimental \( c/a \) and \( V/V_0 \) ratios. The tilt angle was chosen to keep the Ti-F bondlength Eq. 1 constant for all pressure values. We fix \( d_{\text{Ti-F}} = 1.947 \text{ Å} \) and \( d_{\text{Ti-F}} = 1.996 \text{ Å} \) for LDA and LDA+U calculations respectively. For LDA+U calculations \( V_0 \) was fixed to the experimental value \( V_0 = 58.3 \text{ Å}^3 \), while for LDA it is reduced to match the optimal volume \( V_0 = 56.2 \text{ Å}^3 \) to eliminate the strain effects. The results of calculations for the unit cell parameters given in Table I are shown on Fig. 3(b). The high pressure points can be fitted by Eq. 6 to give a bulk modulus of \( B = 42 \text{ GPa} \) for LDA and \( B = 29 \text{ GPa} \) for LDA+U functionals with corresponding coefficients \( K_2 = -0.011 \text{ GPa}^{-1} \) and \( K_2 = -0.008 \text{ GPa}^{-1} \) and optimal volumes \( V/V_0 = 0.86 \) and \( V/V_0 = 0.88 \), which are in agreement with the ambient pressure volume deduced from the high pressure experimental data. The energies in the global minimum in LDA and LDA+U calculations are 270 K and 525 K per TiF\(_3\) lower than that of the experimentally observed structural parameters. A shallower minimum in LDA can be explained by the kinetic energy loss due to the octahedra tilting. In LDA+U the kinetic energy is suppressed due to correlations and does not change much with tilting.

We speculate that this anomalous behavior of the compressibility of TiF\(_3\) may be due to the presence of domain walls in the low symmetry phase observed in 8. Under applied pressure the crystal becomes a single domain. An alternative explanation is the phonon contribution to the free energy which in principle depends on pressure. Additional theoretical calculations of the phonon spectrum and its pressure dependence are needed to estimate the phonon contribution to the bulk modulus anomaly.

![FIG. 8](image_url) Energy difference of the total energy of ferromagnetic and antiferromagnetic solutions as a function of \( U/J \) ratio. The solid line is a second order perturbation theory for the fixed values \( J=0.9 \text{ eV} \) and \( t=0.225 \text{ eV} \). The dots are LDA+U results with fixed \( J = 0.9 \text{ eV} \) and optimal low temperature geometry.

![FIG. 9](image_url) (a) experimental \( P-V \) diagram fitted by the Birch-Murnaghan equation of state to all data points (solid line) and the first six high pressure points (dashed line). (b) bulk modulus calculations using the cell parameters given in Table I. Energies of LDA (LDA+U) calculations are shown by open (filled) circles. The Birch-Murnaghan fit to the high pressure points is shown by the dashed (solid) line for LDA (LDA+U) calculations. The zero energy is chosen at the ambient pressure value.

**TABLE I:** The unit cell parameters for the bulk modulus calculations. The normalized volume \( V/V_0 \) and \( c/a \) ratios are taken from Sowa and Ahsbahs [26]. For LDA+U calculations we used experimental volume \( V_0 = 58.3 \text{ Å}^3 \) at ambient pressure [26], and we choose a smaller \( V_0 = 56.2 \text{ Å}^3 \) for LDA calculations to match the LDA optimal value. For given volume and \( c/a \) ratios the tilt angle was chosen such as Ti-F bondlength Eq. 1 is constant and equal to \( d_{\text{Ti-F}} = 1.947 \text{ Å} \) and \( d_{\text{Ti-F}} = 1.996 \text{ Å} \) for LDA and LDA+U respectively.

| \( p \) (GPa) | \( V/V_0 \) | \( c/a \) | \( \phi^0 \) LDA | \( \phi^0 \) LDA+U |
|-------------|-------------|----------|----------------|----------------|
| 0.0001      | 1.000      | 1.023    | 10.4           | 13.9           |
| 0.46        | 0.957      | 1.056    | 14.3           | 17.0           |
| 1.05        | 0.908      | 1.099    | 17.9           | 20.2           |
| 1.62        | 0.885      | 1.118    | 19.4           | 21.5           |
| 2.37        | 0.864      | 1.138    | 20.8           | 22.8           |
| 3.18        | 0.848     | 1.155    | 21.7           | 23.6           |
| 4.03        | 0.830      | 1.167    | 22.8           | 24.6           |
| 4.97        | 0.818      | 1.181    | 23.5           | 25.3           |
| 6.05        | 0.806      | 1.187    | 24.2           | 25.9           |
| 6.40        | 0.801      | 1.189    | 24.4           | 26.2           |
| 7.23        | 0.793      | 1.193    | 24.9           | 26.6           |
| 7.67        | 0.788      | 1.198    | 25.2           | 26.9           |
VII. CONCLUSION

We used density functional theory to predict the electronic and magnetic properties of TiF$_3$. LDA predicts TiF$_3$ to be a ferromagnetic metal with a fully saturated moment $1\ \mu_B$ per Ti. The energies of the high and the low symmetry structures are degenerate. Such that the pure electron-phonon and electrostatic (Madelung) model does not explain the observed phase transition at $T_c = 370$ K. The correlations are essential to suppress the kinetic energy loss of Ti $t_{2g}$ electrons to favor the distortions. To model electron correlations on Ti $d$ orbitals we use the LDA+U approach, which requires the input parameters $U$ and $J$. We determine these parameters by calculating electron correlations on the TiF$_3^-$ ion and find $U = 8.1$ eV and $J = 0.9$ eV. LDA+U predicts TiF$_3$ to be an antiferromagnetic insulator with spin 1/2 per Ti. We find a long range order of Ti $a_g$ orbitals with a wavevector (000). The low temperature phase is lower in energy by about 900 K per TiF$_3$ in LDA+U calculations, which suggests electron-electron correlations are important.

Using the experimentally determined $c/a$ and $V/V_0$ ratios we find a global minimum at 14% (LDA) and 12% (LDA+U) volumes smaller than the observed ambient pressure volume, which are consistent with the ambient pressure volume deduced from the experimental high pressure data. The experimentally observed larger volume at the ambient pressure and the unusual behavior of the bulk modulus could be understood once the phonon contribution to the free energy is included. The zero phonon energy is in principle pressure dependent and can alter the position of the energy global minimum and the bulk modulus. The Gruneisen parameter calculations and experimental studies of the phonon spectrum under pressure will help to elucidate light to this problem.

Acknowledgments

We are grateful to Fabian Essler for many valuable discussions, Warren Pickett for help in LDA+U calculations, and Dick Watson for useful suggestions. The computations were performed on the BNL galaxy cluster. This work was supported in part by DOE Grant No. DE-AC-02-98CH10886.

[1] D. G. Isaak, R. E. Cohen, M. J. Mehl, D. J. Singh, Phys. Rev. B 47, 7720 (1993).
[2] M. Mochizuki and M. Imada, J. Phys. Soc. Jpn. 70, 2872 (2001).
[3] A. Mogus-Milankovic, J. Ravez, J. P. Chaminade, and P. Hagenmuller, Materials Res. Bulletin 20, 9 (1985).
[4] B. J. Kennedy and T. Vogt, Materials Res. Bulletin 37, 77 (2002).
[5] J. Ravez, A. Mogus-Milankovic, J. P. Chaminade, Mater. Res. Bull. 20, 9 (1985).
[6] P. Daniel, A. Bulou, M. Rousseau, J. L. Fourquet, J. Nouet, M. Leblanc, and R. Burriel, J. Phys. Cond. Matt. 2, 5663 (1990); P. Daniel, A. Bulou, M. Rousseau, J. Nouet, and M. Leblanc, Phys. Rev. B 42, 10545 (1990).
[7] P. B. Allen, Y. R. Chen, S. Chaudhuri, and C. P. Grey (cond-mat/031104).
[8] Y. R. Chen, P. B. Allen, V. Perebeinos, Phys. Rev. B (accepted).
[9] V. I. Anisimov and O. Gunnarsson, Phys. Rev. B 43, 7570 (1991); V. I. Anisimov, J. Zaanen, and O. K. Andersen, Phys. Rev. B 44, 943 (1991).
[10] M. R. Pederson and K. A. Jackson, Phys. Rev. B. 41, 7453 (1990); K. A. Jackson and M. R. Pederson, Phys. Rev. B. 42, 3276 (1990); M. R. Pederson and K. A. Jackson, Phys. Rev. B. 43, 7312 (1991); D. V. Porezag and M. R. Pederson, Phys. Rev. B. 54, 7830 (1996); A. Brey, M. R. Pederson, K. A. Jackson, D. C. Patton, and D. V. Porezag, Phys. Rev. B. 58, 1786 (1998).
[11] I. Solovyev, N. Hamada, and K. Terakura, Phys. Rev. B 53, 7168 (1996).
[12] W. E. Pickett, S. C. Erwin, and E. C. Ethridge, Phys. Rev. B 58, 1201 (1998).
[13] I. V. Solovyev and K. Terakura, Electronic Structure and Magnetism of Complex Materials, ed. by D. J. Singh and D. A. Papakonstantopoulos (Springer, Berlin, 2003).
[14] D. J. Singh, Plane Waves, Pseudopotentials and the LAPW Method (Kluwer Academic, Boston, 1994).
[15] D. J. Singh, Phys. rev. B 43, 6388 (1991).
[16] P. Blaha, K. Schwarz, and J. Luitz, in Proccedings of WIEN97 (Techn. Universitat Wien, Austria, 1999).
[17] J. P. Perdew and Y. Wang, Phys. Rev. B 45, 13244 (1992).
[18] F. D. Murnaghan, Am. J. Math., 49, 235 (1937).
[19] V. I. Anisimov, I. V. Solovyev, M. A. Korotin, M. T. Czyzyk, and G. A. Sawatzky, Phys. Rev. B 48, 16929 (1993); I. V. Solovyev, P. H. Dederichs, and V. I. Anisimov, Phys. Rev. B 50, 16861 (1994); A. I. Liechtenstein, V. I. Anisimov, and J. Zaanen, Phys. Rev. B 52, 5467 (1995); A. B. Shick, A. I. Liechtenstein, and W. E. Pickett, Phys. Rev. B 60, 10763 (1999).
[20] J. C. Slater and G. F. Koster, Phys. Rev. 94, 1498 (1954).
[21] H. Sawada and K. Terakura, Phys. Rev. B 58, 6831 (1998).
[22] Y. Okimoto, T. Katsufuji, Y. Okada, T. Arima, and Y. Tokura, Phys. Rev. B 51, 9581 (1995).
[23] P. W. Anderson, Phys. Rev. 86, 694 (1952).
[24] A. W. Sandvik, Phys. Rev. Lett. 80, 5196 (1998).
[25] T. Vogt et al., unpublished.
[26] H. Sowa and H. Ahsbahs, Acta Cryst. B54, 578 (1998).