

**TiF<sub>3</sub>: Almost nonmagnetic state of a spin- $\frac{1}{2}$  system**R. J. Radwanski<sup>✉\*</sup> and Z. Ropka*Center of Solid State Physics, Snt Filip 5, 31-150 Krakow, Poland*

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We have explained the nonmagnetic state of TiF<sub>3</sub>, down to 10 K, in a strongly-correlated electron approach treating one *d* electron of the Ti<sup>3+</sup> ion as fully localized. We have derived the low-energy states, their energies in the meV energy scale, and their eigenfunctions, considering octahedral crystal-field, trigonal distortion, and spin-orbit interactions. The calculated ground state of the Ti<sup>3+</sup> ion in TiF<sub>3</sub> originates from the *e<sub>g</sub><sup>π</sup>* orbital doublet, contrary to the *a<sub>1g</sub>* orbital singlet reported on the basis of first-principles calculations. The ground Kramers-doublet state is almost nonmagnetic due to compensation of the spin and orbital momenta. Our approach reveals the fundamental importance of intra-atomic relativistic spin-orbit coupling for calculations of the magnetism and the electronic structure of 3*d* fluorides/oxides, pointing out that strong electron correlations are predominantly of a local on-site origin.

DOI: [10.1103/PhysRevB.109.155148](https://doi.org/10.1103/PhysRevB.109.155148)**I. INTRODUCTION**

The transition-metal fluoride empty perovskites *BF<sub>3</sub>* (an empty *A* site in the perovskite *ABO<sub>3</sub>*) up to now have been largely studied due to their unique negative (or zero) thermal expansion (NTE or ZTE) properties [1–3]. It is believed that their ground state resides very close to a structural quantum phase transition between a (high-temperature) cubic high-symmetry *Pm $\bar{3}$ m* and lower-symmetry rhombohedral *R $\bar{3}$ c* structure (space group No. 167) which is nicely visible in Sc<sub>*x*</sub>Ti<sub>1–*x*</sub>F<sub>3</sub> systems, in which the transition temperature increases from *T* = 0 K in ScF<sub>3</sub> to 340 K in TiF<sub>3</sub> [1,3].

In a very recent paper, Sheets *et al.* [1] show that, despite one extra electron in TiF<sub>3</sub> compared to ScF<sub>3</sub>, TiF<sub>3</sub> is still an insulator, contrary to the ferromagnet half metal derived in an earlier theoretical work of Perebeinos and Vogt [2] in an uncorrelated (*U* = 0) limit.

It seems that the paper of Sheets *et al.* is the only one presenting the magnetic properties of TiF<sub>3</sub>. By revealing the Curie-Weiss behavior in the 20–60 K range with an effective Ti moment of 1.40  $\mu_B$  and  $\theta_{CW} = -13.8$  K, these authors concluded that “correlated electron physics” is required for a consideration of the electronic and magnetic properties of TiF<sub>3</sub>. This correlated electron physics yielded in their Fig. 4 an electronic density of states (DOS) for TiF<sub>3</sub> in a quite schematic eV energy scale for three different values of the electronic correlation parameter *U* and *J* as (0, 0), (3, 0.2), and (6 and 0.5 eV). All these sets separate well the fluorine 2*p* states 5–9 eV below the Fermi level. The last set of parameters separates the one-electron DOS from the other 3*d* states. It has been attributed to the *a<sub>1g</sub>* orbital originating from the Ti octahedral *t<sub>2g</sub>* band of about 2 eV width, confirming the earlier results of Ref. [2] yielding *U* = 8.1, *J* = 0.9, *t* = 0.25 eV, and the antiferromagnetism with *S* =  $\frac{1}{2}$ . To our knowledge,

Refs. [1,2] are the only ones devoted to electronic structure calculations of the 3*d*-electron states in TiF<sub>3</sub>.

The sister isoelectronic chlorides TiCl<sub>3</sub> and ZrCl<sub>3</sub> have been theoretically studied in the search for practical realizations of different quantum spin liquids [4–6]. Earlier, other 3*d*<sup>1</sup> systems, such as Sr<sub>2</sub>VO<sub>4</sub> and LaTiO<sub>3</sub>, have been studied in the search for an orbital liquid [7,8].

In our work we claim that calculations of the electronic structure for 3*d* states in TiF<sub>3</sub> have to be performed in the meV energy scale, not in the eV energy scale. Such a meV energy scale is necessary for the structural phenomena occurring in TiF<sub>3</sub> at 340 K (a thermal energy of 30 meV). The authors of Ref. [1] have observed a small cusp in the  $\chi(T)$  curve of TiF<sub>3</sub> at 10 K (1 meV) attributing it to an appearance of antiferromagnetism. We feel that TiF<sub>3</sub>, due to its structural simplicity and only one 3*d* electron, will largely help in an overall understanding of the 3*d* magnetism and the detailed low-energy electronic structure of 3*d*-ion containing compounds.

**II. THEORETICAL OUTLINE**

In deriving the electronic structure of TiF<sub>3</sub> we will exploit the experimental fact that TiF<sub>3</sub> does not show any clear magnetic ordering down to 10 K—we will try to attribute this experimental fact not to the weakness of spin-spin interactions but to a small local Ti magnetic moment despite the Ti<sup>3+</sup> ion, having one electron in the open 3*d* shell, has spin- $\frac{1}{2}$ .

In our approach the on-site crystal-field and spin-orbit (SO) interactions are fundamentally important, realizing our 40-yr general scientific concept from atomic physics to solid-state physics [9].

In our approach, which we call the quantum atomistic solid-state theory (QUASST), the magnetic and electronic properties of open-shell oxides are largely determined by a single-ion electronic structure determined by crystal-field and spin-orbit interactions [9–11]. Crystalline electric field (CEF)

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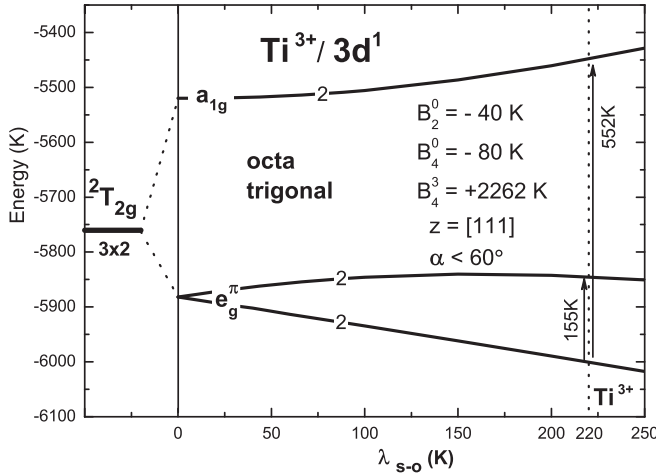


FIG. 1. The calculated extra effect of the spin-orbit ( $\lambda_{so}$ ) interactions on the  $t_{2g}$  triplet states, split by the trigonal stretched off-octahedral distortion (measured by a  $B_2^0$  CEF parameter of  $-40$  K) in the presence of an octahedral crystal field ( $B_4^3 = +120$  K).  $\lambda_{so}$  of  $+220$  K is relevant to the  $Ti^{3+}$  ion. The distortion and SO energy effects are of comparable size. Zero energy is at the two Hund's rules  $^2D$  term energy. The magnetic moment of the lowest Kramers doublet is very small, of  $\pm 0.06 \mu_B$  for  $\lambda_{so} = 220$  K, due to the cancellation of the spin moment by the orbital moment.

interactions result from charge interactions of the given paramagnetic ion in the crystal with its charge surroundings. A benchmark of the CEF + SO-based QUASST is the integer valency of the involved transition-metal ion and the “survival” of this discrete low-energy meV electronic structure in  $3d/4f/5f/4d/5d$  compounds, both ionic and intermetallic. Magnetism develops on these discrete low-energy meV electronic structures [9,11]. For  $3d$ -ion compounds we can mention the description of  $FeBr_2$  [11] and  $CoF_3$  [12]. As an ionic compound with a  $3d^1$  configuration we mention  $BaVS_3$ , where we have pointed out the fundamental importance of the SO interactions even in  $3d$  ions manifested by the substantial cancellation of the spin moment by the orbital moment [13,14]. In all these last three ionic compounds the  $3d$  ions are in a local trigonally distorted octahedral-symmetry crystal field.

### III. RESULTS AND DISCUSSION

In  $TiF_3$  the  $Ti^{3+}$  ions are in fluoride octahedral surroundings with a small trigonal distortion [along the original (primary) cube diagonal] appearing in a rhombohedral structure. A similar rhombohedral symmetry occurs for the sister system  $CoF_3$ , whose low-energy meV electronic structure and magnetic properties we have analyzed earlier in Ref. [12]. The CEF + SO Hamiltonian for the  $3d^1$  states of the  $Ti^{3+}$  ion is the same as we have used for other systems with trigonal local symmetry:  $FeBr_2$  [11],  $CoF_3$  [12], and  $BaVS_3$  [13].

The effect of the octahedral CEF is widely known—it splits five orbital states ( $L = 2$ ) into a lower orbital triplet  $t_{2g}$  and a higher orbital doublet  $e_g$  separated by  $10Dq (= 120B_4^0)$  [15]. The lower orbital triplet  $t_{2g}$  is split by the distortion ( $B_2^0$ ) into an orbital doublet (denoted as  $e_g^\pi$ —a quartet in the spin-orbital space) and a higher orbital singlet denoted as  $a_{1g}$  (Fig. 1). As

the splitting  $10Dq$  is usually larger than 1 eV, discussions in the literature are often limited to the  $t_{2g}$  states [7]. Then calculations are performed within the sixfold basis with effective  $\tilde{L} = 1$  and  $S = 1/2$  [7]. We perform calculations within the full two Hund's rules atomic term, in the  $(2L+1)(2S+1)$ -fold space, in the case of a  $Ti^{3+}$  ion within the  $^2D$  term ( $L = 2$  and  $S = 1/2$ ).

In Ref. [10] we have calculated the electronic structure resulting from the action of the spin-orbit interactions in the presence of octahedral crystal-field interactions for the  $d^n$  ions, with  $n = 1$  ( $Ti^{3+}$  or  $V^{4+}$ ) to  $n = 9$  ( $Cu^{2+}$  or  $Ni^{1+}$ ) configurations (see Fig. 1 of Ref. [10]). The realized magnetic moment is written on the states. It is worth noting the zero moment for the ground state for the  $d^1$  configuration. It is exactly the local  $Ti$  state that we are looking for as the physical reason for the nonmagnetic state of the whole compound  $TiF_3$ .

In Fig. 1 we show the effect of spin-orbit interactions on a  $t_{2g}$  states split by trigonal distortion, expressed by the  $B_2^0$  parameter. With trigonal off-octahedral distortion, realized for  $B_2^0 < 0$ , this nonmagnetic (or, in other words, a very weakly magnetic) state becomes the ground state. It is necessary to remember that it is a spin (Kramers) doublet. A negative value of  $B_2^0$  results from the observed elongated trigonal distortion, seen in the trigonal angle  $\alpha < 60^\circ$  in the description of the  $R\bar{3}c$  structure. The angle  $\alpha$  amounts to  $56.97^\circ$  and  $57.99^\circ$  in  $CoF_3$  and  $FeF_3$ . Thus our calculations and analysis of the lattice distortion have revealed that the ground state of  $Ti^{3+}$  in  $TiF_3$  originates from the  $e_g^\pi$  orbital doublet, contrary to the  $a_{1g}$  orbital singlet reported on the basis of the first-principles calculations in Refs. [1,2].

The spin-orbit interactions split the  $t_{2g}$  triplet for three Kramers doublets (Fig. 1). The parameters shown in Fig. 1 seem to be realistic. The value of  $10Dq$  of 1.25 eV is related to a  $B_4^0$  of  $+120$  K. This  $B_4^0$  value could be smaller, being close to a value of  $+90$  K obtained from our analysis of the sister fluoride  $CoF_3$  [12]. Also, the distortion parameter in  $TiF_3$  of  $-40$  K is close to  $-25$  K derived for  $CoF_3$ . It is worth noting that all three parameters have a clear physical meaning and produce clear physical effects.

The lowest Kramers doublet is characterized by a small total magnetic moment despite the almost full spin magnetic moment expected from  $S = \frac{1}{2}$ . Namely, for a value of  $\lambda_{so}$  of  $+220$  K relevant to the  $Ti^{3+}$  ion, the eigenfunction of the ground-state Kramers doublet takes the form (only  $L_z$  and  $S_z$  values  $|LSL_zS_z\rangle$  are shown from  $L = 2$  and  $S = 1/2$ )

$$\psi_{GS} = 0.829|\pm 2, \mp 1/2\rangle \mp 0.558|\mp 1, \mp 1/2\rangle. \quad (1)$$

This function yields a total moment of the ground-state doublet of  $\pm 0.06 \mu_B$  built from the orbital moment of  $\pm 1.06 \mu_B$  and of the spin moment  $\mp 0.998 \mu_B$ . So, due to (positive) spin-orbit coupling there is almost a full cancellation of the spin moment by the orbital moment. The excited four doublet states are at energies of 155, 550, 14 640, and 14 647 K. Thus the width of the  $t_{2g}$  “band” is only 50 meV. The full spread of the  $3d$  “band” is 1.25 eV.

The first excited orbital ( $e_{g2}$ ) at 155 K (14 meV) has the form

$$\psi_{ex1} = 0.732|\pm 2, \pm 1/2\rangle \mp 0.525|\mp 1, \pm 1/2\rangle \pm 0.435|0, \mp 1/2\rangle, \quad (2)$$

and is characterized by a total magnetic moment  $\pm 1.42 \mu_B$  built by an orbital moment of  $\pm 0.80 \mu_B$  and by a spin moment  $\pm 0.62 \mu_B$ .

The second excited orbital ( $a_{1g}$ -like) at 550 K has the form

$$\psi_{\text{ex2}} = 0.900|0, \pm 1/2\rangle + 0.363|\mp 2, \mp 1/2\rangle + 0.239|\pm 1, \mp 1/2\rangle, \quad (3)$$

and is characterized by a total magnetic moment  $\pm 0.42 \mu_B$  built by an orbital moment of  $\mp 0.20 \mu_B$  and by a spin moment  $\pm 0.62 \mu_B$ .

In the shape of the eigenfunction Eq. (1) one finds indications of the total angular momentum  $J_{\text{eff}} = 3/2$  (the sum of  $L_z$  and  $S_z$ , being opposite, gives 1.5) realized in the case of strong spin-orbit coupling, though the calculated resultant  $J_z$  is only  $\pm 0.56$ . Similarly, the  $a_{1g}$ -like state of Eq. (3) still preserves 90% of the CEF  $a_{1g}$  function, though the calculated resultant  $J_z$  is only  $\pm 0.10$  instead of  $J_{\text{eff}} = 1/2$ .

The trigonal distortion and SO energy effects are of comparable size, of 360 and 330 K, respectively. It causes these two interactions to have to be treated on the same footing, making theoretical calculations troublesome.

Our CEF-based QUAASST approach is a strongly correlated electron approach with a fully localized one  $d$  electron in the incomplete  $3d$  shell of the  $\text{Ti}^{3+}$  ion. The full localization, used in the CEF approach, means that  $U = \infty$ , which completely prohibits the double occupancy of the lowest Kramers doublet. The authors of Refs. [1,2], in deriving  $U = 6.5$  or  $8.1$  eV, do not say anything about the effect in their calculations when taking other  $U$  values. Rationally thinking, one would expect that 8 eV, being equivalent to a thermal energy of almost 100 000 K, yields the probability of the double occupancy to be of order of  $e^{-1000}$  at 100 K. In our approach we say that the probability is exactly zero and in our approach double occupancy is simply forbidden. Our results about the electronic structure can be treated as a low-energy complement to the high-energy results of Refs. [1,2]. Similarly, our present work and the CEF-QUASST approach extend calculations of the spin moment of Refs. [1,2] for the orbital moment and the very detailed electronic structure.

QUASST deals with allowed low-energy excitations. Thus the obtained ionic ground state coincides with the Fermi level for excitations of itinerant electrons.

QUASST allows calculations of the orbital magnetic moment. We have found in  $\text{TiF}_3$  a very substantial orbital magnetic moment, close to  $1.0 \mu_B$ . In  $\text{NiO}$ , describing the low-energy electronic structure and magnetic properties, we have derived an orbital moment of  $0.54 \mu_B$  [16]. One would be very surprised after much education and learning in many solid-state magnetic textbooks, of, e.g., Kittel's solid-state

textbook, that the orbital moment in  $3d$  ions is quenched. It is true, but it is quenched provided that the orbital state is not degenerated. In the  $\text{Ti}^{3+}$  ion the orbital moment appears because here we have a situation with an orbital doublet ground state or/and two (or many) closely lying orbital states.

Finally, we are awaiting further experimental studies of  $\text{TiF}_3$ . We would suggest the temperature dependence of the magnetic susceptibility in a wider temperature region than shown in Fig. 3 of Ref. [1] above 60 K, even on a powder polycrystalline sample. Of course, it would be better if studies were conducted on a single-crystalline sample. Then our model could be further verified because it predicts highly anisotropic  $\chi(T)$  dependences related to the rhombohedral structure.

The second type of experiments we would propose are at a low-temperature specific heat below 10 K—then our model predicts a large low-temperature heat resulting from the removal of the Kramers degeneracy of the weakly magnetic ground state.

#### IV. CONCLUSIONS

We have derived, within the strongly correlated electron approach with a fully localized one  $d$  electron in the incomplete  $3d$  shell of the  $\text{Ti}^{3+}$  ion, a low-energy electronic structure, in the meV energy scale, considering crystal-field and intra-atomic relativistic spin-orbit interactions. The obtained spin-orbital Kramers-doublet ground state of the  $\text{Ti}^{3+}$  ion is practically nonmagnetic due to the almost perfect compensation of the spin and orbital momenta preventing the development of any spin-magnetic interactions down to temperatures of 10 K. The calculated ground state of the  $\text{Ti}^{3+}$  ion in  $\text{TiF}_3$  originates from the  $e_g^\pi$  orbital doublet, contrary to the  $a_{1g}$  orbital singlet reported on the basis of the first-principles calculations in Refs. [1,2].

The derived single-ion weakly magnetic state of the  $3d^1$  ion is in strong contrast to the spin-liquid description due to the exchange frustration in triangular lattices [17] or by the formation of a nonmagnetic disordered spin-orbit dimer phase in  $5d^1$  cubic double perovskites [18]. We have applied our QUASST approach to the  $4d^1$  ion in the successful single-ion  $\text{Mo}^{5+}$  description of the temperature dependence of the paramagnetic susceptibility in the double-perovskite  $\text{Ba}_2\text{YMoO}_6$  [19], deriving a low-energy crystal-field-like discrete electronic structure.

Our calculations indicate the fundamental importance of intra-atomic spin-orbit interactions and lattice distortions for the magnetism and the low-energy electronic structure in other  $3d$  fluorides/oxides, pointing out that strong electron correlations are predominantly of a local on-site origin.

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