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Really First Principles Calculations for CoF_3

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We have derived the low-energy electronic structure of CoF_3, originating from the strongly-correlated $3d^6$ system of the Co^{3+} ion, taking into account the crystal-field interactions, with a relatively weak trigonal distortion, and the relativistic spin–orbit interaction. We have calculated from really first-principles the relevant crystal-field interactions. With the discrete electronic structure for $3d$ electrons we have described the magnetic properties (the value of the magnetic moment and its direction). The moment direction is determined by the local off-octahedral trigonal distortion proving the single-ion origin of the magnetocrystalline anisotropy. We evaluated the orbital moment and the strength of spin interactions responsible for the formation of the magnetic state. Our studies indicate that calculations of the electronic structure of a $3d$ compound for the physically-adequate description of the magnetic properties has to be performed at the meV scale.

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1. Introduction

CoF_3 is one of compounds with the trivalent Co ions. Years ago it was believed that compounds with the trivalent Co ions are all nonmagnetic [1]. $LaCoO_3$ is very profound example of such situation [2]. In this respect the existence of the strong magnetism in CoF_3, with $T_N = 460$ K, is surprising [3]. In 2003 we have evaluated the electronic structure of $LaCoO_3$ and the origin of the non-magnetic ground state as due to very strong crystal-field interactions and onsite formation of the $^1A_1$ singlet ground state originating from the ^1I atomic Co^{3+} term [4].

CoF_3 crystallizes in the rhombohedral crystallographic structure with $a = 527.9$ pm and the angle $\alpha = 56.97$ degrees [3]. The magnetic moment of a value close to 5 μ_B (4.4 μ_B) lies along the trigonal axis [5]. Below T_N of 460 K the magnetic moments form ferromagnetic planes which orders antiferromagnetically along the trigonal axis.

The aim of this paper is to present a consistent understanding of magnetic properties of CoF_3 within the localized atomistic paradigm. Here we concentrate on the value and the direction of the magnetic moment in correlation to the crystallographic structure. In our understanding we have employed well-known physical concepts like strong electron correlations, the crystal-field (CEF) interactions, spin–orbit (s-o) coupling and local distortions.

2. Theoretical outline

Although we are fully aware about complex solid-state theories we understand CoF_3, at least at the beginning, as a purely ionic compound. During the formation of this compound there proceeds the charge transfer of three electrons from each Co atom to the fluoride atoms establishing the ionic charge distribution $Co^{3+}F_3^{1-}$. Thanks it the monovalent fluoride anions are formed with the completed $2p$ shell. Due to this we do not expect any magnetism, apart from a small diamagnetic contribution, from fluorides. Left six electrons of the Co^{3+} ion outside the ^{18}Ar configuration form a strongly-correlated atomic-like system, $3d^6$. The two Hund rules yield the ^5D ground term, which is 25-fold degenerated, Fig. 1. For describing the Co^{3+} ion behavior we have applied a Hamiltonian in a form

$$H = H_{CF} + H_{s-o} + H_{d-d} = \sum_{n,m} B_n^m \widehat{O}_n^m(L, L_z) + \lambda_{s-o} LS + n_{d-d}\mu_B^2 \left(-m_d\langle m_d\rangle + \frac{1}{2}\langle m_d\rangle^2\right) + \mu_B(L + g_e S)B_{ext} \tag{1}$$

For the ^5D term of the Co^{3+} ion $L = 2$ and $S = 2$. m_d denotes the magnetic moment of the Co^{3+} ion (in the μ_B units) and is built as $L + g_e S$ with $g_e = 2.0023$. λ_{s-o} is the spin-orbit coupling like in the atomic physics ($\lambda_{s-o} = -140$ K).

In CoF_3 there is only one Co site described as the $2b$ site in the $R\bar{3}c$ structure (SG 167) or as the $6b$ site in the hexagonal description.

3. Results and discussion

The rhombohedral lattice parameters $a = 527.9$ pm and angle $\alpha = 56.97$ degrees (Co(2b) — 0,0,0 and 1/2,1/2,1/2, and the F(6e) site is characterized by $x = -0.15$ [4]) correspond to the hexagonal-cell parameters $a = 503.5$ pm and $c = 1321.8$ pm with six formula units instead of two in the rhombohedral cell. In the hexagonal cell Co occupy the 6b site 0,0,0 and 0,0,1/2, whereas the F anions occupy the 18e site with the free parameter $x = 0.60$.

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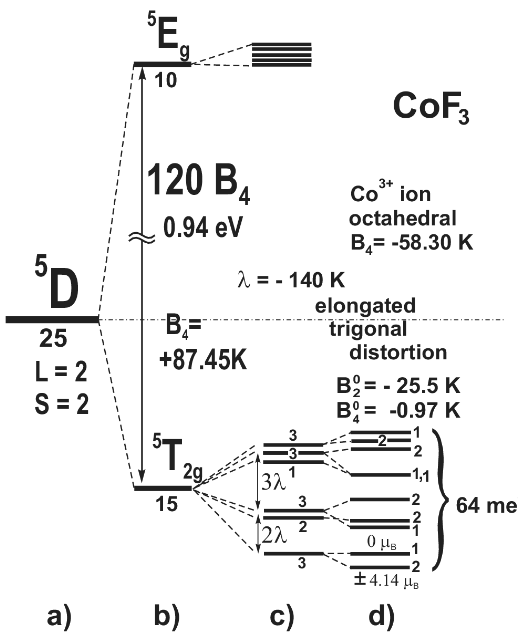

Fig. 1. The fine electronic structure of the highly-correlated $3d^6$ electronic system of the Co^{3+} ion in CoF$_3$: (a) the 25-fold degenerated ^{5}D term given by Hund's rules: $S = 2$ and $L = 2$. (b) the effect of the octahedral crystal-field, (c) the combined action of the spin-orbit coupling and the octahedral crystal field: $B_4 = +87$ K, $\lambda = -140$ K; (d) further splittings due to distortions (1 meV = 1.6 K).

The local symmetry of the Co ion is predominantly octahedral — the Co ion is surrounded by six nearest neighbours fluorines forming almost perfect octahedron with $d_{\mathrm{Co}-F} = 189$ pm. In the rhombohedral structure the main diagonal of the local octahedron is along the trigonal symmetry axis. Such situation allows for the trigonal off-octahedral distortion. From the lattice parameters one concludes that this trigonal distortion is of the elongated type.

Thus the symmetry-allowed crystal-field parameters are B_4 (dominant octahedral interactions), and those from the trigonal distortion $B_2^{0,t}$ and $B_4^{0,t}$.

In the crystal-field theory the octahedral parameter $10Dq$ ($\cong 120B_4$) in the simplest form is the multiplication of the hexadecapolar charge moment of the lattice A_4 (thus A_4 is a measure of the charge distribution of the given cation) and of the involved cation due to anisotropic charge distribution of the own incomplete ($3d$) shell. Thus Dq (B_4) can be calculated from first principles provided the atomic-like hexadecapolar charge moment, $\beta\ \langle r_d^4\rangle$, of the involved ion is known. β is the fourth-order Stevens coefficient.

The octahedral crystal-field coefficient A_4, the hexadecapolar charge moment of all surrounding charges at the Co site, we have calculated from the point-charge model (really first-principles calculations) taking the charge of fluorine as $-1e$ and the cation–oxygen distance of 189 pm in CoF$_3$. We have obtained a value of A_4 of $+235$ Ka_{B}^{-4}, a_{B} is the Bohr radius. Taking for the Co^{3+} ion $\beta = +2/63$ and $\langle r_d^4\rangle = 11.71\ a_{\mathrm{B}}^4$ we get $B_4 = +87.45$ K. This value yields the $t_{2\mathrm{g}}$–e_{g} splitting ($10Dq$) in CoF$_3$ of 0.90 eV situating CoF$_3$ in the weak crystal-field regime on the Tanabe–Sugano diagram [6]. It means that six d electrons of the Co^{3+} ion takes the high-spin $t_{2\mathrm{g}}^4 e_{\mathrm{g}}^2$ ($S = 2$) configuration.

Point-charge calculations of the effect of the off-octahedral distortion yield the parameter $B_2^0 = -25.5$ K, with $\langle r_d^2\rangle = 1.521$ a$_{\mathrm{B}}^2$), and extra $B_4^{0,t} = -0.97$ K (here z axis is along the main diagonal, then the relevant dominant hexadecapolar crystal-field parameter B_4 equals –58.30 K). The trigonal distortion is relatively small but it causes a slight splitting of the lowest quasi-triplet by $\Delta = 23$ K with the lowest doublet, see Fig. 2. It turns out that this trigonal distortion determines the direction of the magnetic moment in the magnetically-ordered state below T_{N} of 460 K, i.e. the trigonal elongation orients the moment along the main local octahedral diagonal.

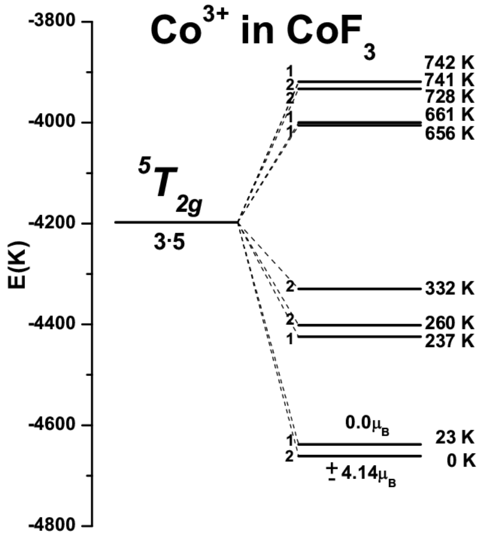

Fig. 2. The lowest electronic structure of the highly-correlated $3d^6$ electronic system of the Co^{3+} ion in CoF$_3$ in the paramagnetic state; the trigonal-distortion parameter $B_2^0 = -25.5$ K produces a spin-like gap of 2 meV; the double degeneracy of the ground state is removed in the magnetically-ordered state below T$_N$ of 460 K.

Following the way of calculations like we have performed for FeBr$_2$ [7] we reproduce the value of 460 K for T_{N} by n_{dd} value of 62.2 T/μ_{B}. Self-consistent calculations yield the total magnetic moment at $T = 0$ K of 5.11 μ_{B}. It is composed from the spin moment of 3.95 μ_{B} and the orbital moment of 1.16 μ_{B}. At zero temperature the molecular field acting on the Co moment amounts to 318 T. The derived electronic structure in the magnetic state, shown in Fig. 3, yield the temperature dependence of the heat capacity with

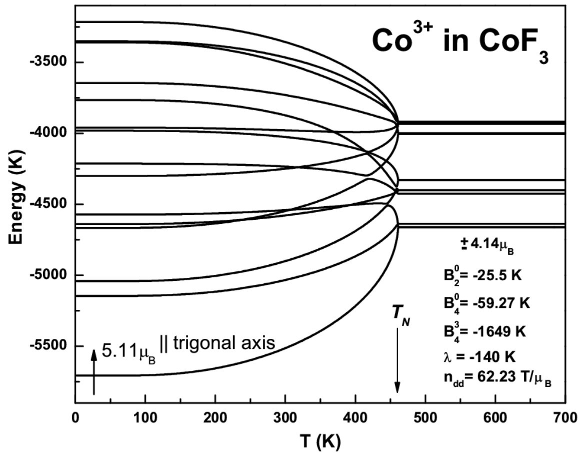

Fig. 3. The electronic structure of the Co^{3+} ion in CoF_3 in the magnetically-ordered state below T_N of 460 K.

the λ-type peak at 460 K and the temperature dependence of the magnetic susceptibility with p_{eff} of 5.34 μ_B (in the interval of 600–800 K). This value is close to the typical experimental value for the high-spin Co^{3+} compounds.

We would like to note that all of the used by us parameters (dominant octahedral CEF parameter B_4, the spin-orbit coupling λ_{s-o}, lattice distortions) have clear physical meaning and can be calculated from the really first principles. The most important assumption is the existence of very strong correlations among $3d$ electrons preserving the atomistic ionic integrity [8] of the Co^{3+} ion also in the crystalline solid when this cation becomes the full part of a crystalline solid in CoF_3. The obtained good description of CoF_3 provides the further evidence that the low-energy discrete electronic structure of the transition-metal atom predominantly determines the macroscopic properties of the whole compound containing transition-metal $3d/4f/5f$ atoms.

Finally, our description of CoF_3 is fully consistent with $LaCoO_3$ [4], $FeBr_2$ [7] and FeO [9]. Despite the fact that all these three compounds have different crystallographic structure they have local octahedra around Co/Fe cations. These octahedra are compressed in case of $LaCoO_3$ and elongated in case of $FeBr_2$ and FeO (like here for CoF_3). This compression and elongation is seen in the sign of the B_2^0 parameter (positive in $LaCoO_3$ and negative in case of $FeBr_2$). One should notice that the Fe^{2+} ion and the Co^{3+} ion are isoelectronic being the $3d^6$ quantum systems.

4. Conclusions

We have calculated from really first principles the low-energy electronic structure of CoF_3 which determines its macroscopic properties. The electronic structure originates from the Co^{3+} ions experiencing dominant octahedral crystal-field interactions, the intra-atomic spin–orbit coupling and a relatively weak trigonal distortion. Our calculations explain the strongly-magnetic ground state, as related to the ionic high-spin ${}^5T_{2g}$ subterm (from the atomic ${}^5D$ term), and the insulating ground state. We have derived a large orbital contribution to the magnetic moment (1.16 μ_B). Our model explains both the zero-temperature properties and thermodynamics. The moment direction is determined by the local off-octahedral trigonal distortion proving the single-ion origin of the magnetocrystalline anisotropy. Our long-lasting studies as well as growing number of more and more sophisticated experiments indicate that it is the highest time to "unquench" the orbital moment in the solid-state physics for the adequate theoretical description of the magnetism and the electronic structure of $3d$-atom containing compounds.

We carefully analyse some cases to reveal scientific reasons for a claim of the failure of the point-charge model. Only step by step, compound by compound considerations can reveal the applicability and shortages of the point-charge model and the crystal-field theory.

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