

Universal metastability of the low-spin state in Co^{2+} systems: Non-Mott type pressure-induced spin-state transition in CoCl_2

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(Received 19 December 2012; revised manuscript received 15 March 2014; published 27 March 2014)

We have investigated the pressure-induced spin-state transition in Co^{2+} systems in terms of a competition between Hund's exchange energy (J) and crystal-field splitting (Δ_{CF}). First, we show the universal metastability of the low-spin state in octahedrally coordinated Co^{2+} systems. Then we present the strategy to search for a Co^{2+} system, for which the mechanism of spin-state and metal-insulator transitions is governed not by Mott physics but by J versus Δ_{CF} physics. Using CoCl_2 as a prototypical Co^{2+} system, we have demonstrated the pressure-induced spin-state transition from high-spin to low-spin, which is accompanied with insulator-to-metal and antiferromagnetic to half-metallic ferromagnetic transitions. Combined with the metastable character of Co^{2+} and the high compressibility nature of CoCl_2 , a transition pressure as low as 27 GPa can be identified on the basis of J versus Δ_{CF} physics.

DOI: [10.1103/PhysRevB.89.115131](https://doi.org/10.1103/PhysRevB.89.115131)

PACS number(s): 71.30.+h, 71.15.Mb, 71.70.Ch, 75.30.Wx

The spin-state transition in transition-metal (TM) complexes has been a subject of intense study. The stabilization of one spin state over another is determined by the competition of various energy scales, such as Coulomb correlation (U), bandwidth (W), Hund's exchange energy (J), crystal-field splitting (Δ_{CF}), and so on. Pressure induces the spin-state transition by changing the relative strength of different energy scales, especially either W or Δ_{CF} . In many cases, the pressure-induced spin-state transition is accompanied by the metal-insulator transition, which can be well described with either the J/Δ_{CF} or U/W ratio. In real systems, both are important and interconnected. The physics of J versus Δ_{CF} is hard to explore in a typical pressure study due to the entrance of U versus W physics in the form of d - p hybridization or crystal distortion. In a simple TM monoxide, e.g., MnO , as pressure increases, the change of Δ_{CF} plays a primary role in the high-spin (HS) to low-spin (LS) state transition and the insulator-to-metal transition. However, the underlying physics is governed not only by J and Δ_{CF} but also U and W , and even by the charge-transfer energy ($\Delta_{\text{CT}} = \varepsilon_d - \varepsilon_p$), which all take part in the process of the spin-state transition [1].

Studies of the spin-state transition in Co-containing complexes have been mostly concentrated on the Co^{3+} (d^6) systems. A well-known example is perovskite LaCoO_3 . LaCoO_3 exhibits a temperature-dependent spin-state transition, which can be interpreted as LS ($S = 0$) to HS ($S = 2$) or LS to intermediate-spin (IS) ($S = 1$) transition. The exact magnetic phase and the underlying mechanism are, however, still under debate [2–6]. Since the energy scales J and Δ_{CF} in LaCoO_3 are similar, thermal excitation can easily mix or switch different spin states in cooperation with lattice distortion [3]. Recently, Kuneš *et al.* [6] presented the spin-state transition in terms of a purely electronic origin without the lattice effect. Also, for LaCoO_3 , it is known that pressure produces a similar effect to temperature, which is described as the depopulation of an IS state rather than phase change [7–10].

In contrast to Co^{3+} systems, the spin-state transition in Co^{2+} (d^7) systems is relatively unexplored. This is because most Co^{2+} systems have stable HS ($S = 3/2$) states. Nevertheless, the HS-LS transitions have been discussed for

a few Co^{2+} systems, such as organic complexes [11–15], YBaCo_2O_5 [16,17], CoCl_2 [18], and $\text{Ca}_3\text{Co}_{2-x}\text{Mn}_x\text{O}_6$ [19]. In particular, for CoCl_2 , the pressure-induced metallization driven by the spin-state transition was indicated by carrying out high-pressure optical-absorption measurements [18]. But the isostructural spin-state transition in Co^{2+} systems has not been confirmed experimentally and theoretically yet.

Motivated by the above investigations of the spin-state transition for Co^{3+} systems, we have studied the energetics of different spin states of various octahedrally coordinated Co^{2+} (CoX_6) systems on the basis of the *ab initio* electronic-structure calculations. Their magnetic properties are described by Co^{2+} ions, which have HS $3d^7$ ($t_{2g}^5 e_g^2$) configurations in the ground state. Interestingly, all the tested systems have LS ($S = 1/2$) metastable states, and moreover their HS-LS energy differences are of almost the same scale, independent of the anion (X) type, Co- X bond length, and CoX_6 octahedron distortions. We then discuss the strategy of searching for materials having the pressure-driven spin-state transition governed by J versus Δ_{CF} physics, unlike other TM oxides that show the Mott-type transition governed by U and W . We propose that CoCl_2 is a prototypical Co^{2+} system having J versus Δ_{CF} physics. We show that CoCl_2 has abrupt collapses in volume and spin magnetic moment at the spin-state transition point, which is also accompanied by the insulator-to-metal transition.

To investigate the spin-state transition in Co^{2+} systems, we have performed electronic-structure calculations employing the full-potential linearized augmented plane wave (FLAPW) band method [20] implemented in WIEN2K [21]. Since the often-used pseudopotential band method is known to have problems in describing the spin states under volume reduction, the application of the full-potential band method is essential in the pressure studies [22]. For the exchange-correlation energy functional, we used the generalized gradient approximation (GGA) with the PBEsol functional [23]. On-site Coulomb correlation is treated with the GGA + U method in the rotationally invariant form [24,25]. Spin-orbit coupling (SOC) was included in the second variational scheme when necessary.

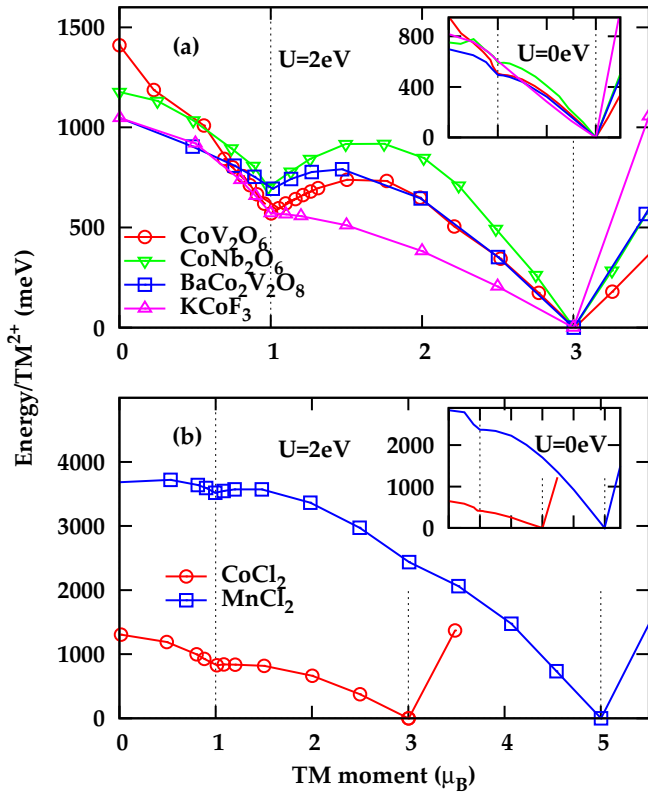


FIG. 1. (Color online) Energy vs spin magnetic moment obtained by using the FSM calculation. (a) For octahedrally coordinated Co²⁺ systems: α -CoV₂O₆, CoNb₂O₆, BaCo₂V₂O₈, and KCoF₃. (b) For two dichlorides: CoCl₂ and MnCl₂. Results in the GGA + U scheme with $U = 2$ eV are shown. Insets are for $U = 0$. Spin magnetic moment is obtained by dividing the total magnetic moment by the number of Co ions in the system to include the induced magnetic moment.

We first identify the general metastability of LS phase in the octahedrally coordinated Co²⁺ systems. We have carried out the fixed-spin moment (FSM) calculations for various Co²⁺ systems, including chain-type brannerite α -CoV₂O₆ [26] and CoNb₂O₆ [27], complex chain-tetragonal BaCo₂V₂O₈ [28], cubic perovskite-type cobaltate fluoride KCoF₃ [29], and simple layered rhombohedral cobaltate dichloride CoCl₂ [30]. All the above systems have Co as the only magnetic ion. Figure 1(a) shows the energy versus spin magnetic moment for those Co²⁺ systems. In addition to the global ground HS states at the moment (M) of $3\mu_B/\text{Co}^{2+}$, we can clearly see the metastable LS states at $M = 1\mu_B/\text{Co}^{2+}$ for all cases. Furthermore, the HS-LS energy differences (ΔE 's) are almost the same. ΔE 's are 400–600 and 570–830 meV for $U = 0$ and 2.0 eV, respectively. The inclusion of U tends to increase ΔE because the HS state is more favored with larger U . However, the universal metastability of the LS phase remains the same.

The similarity in the energy scale of ΔE for different systems is striking because in addition to the macroscopic crystal structure, the local CoX₆ ($X = \text{O}, \text{F}, \text{and Cl}$) octahedron structure is also quite different from system to system. For example, the Co- X bond length is very short for KCoF₃ (2.03 Å), but very long for CoCl₂ (2.42 Å), even though both have almost ideal octahedra. CoNb₂O₆ and BaCo₂V₂O₈ have

tetragonal distortions, and α -CoV₂O₆ has additional in-plane rectangular distortion that produces extraordinary crystal-field levels [31]. This feature suggests that the metastability of LS phase is robust in the octahedrally coordinated Co²⁺ systems.

In a simplified picture, the energy difference between the LS ($t_{2g}^6 e_g^1$) and the HS ($t_{2g}^5 e_g^2$) state can be expressed as

$$\Delta E = E_{\text{LS}} - E_{\text{HS}} = 2J - \Delta_{\text{CF}}. \quad (1)$$

Because Hund's exchange J does not have much system dependence, the similar ΔE value for all systems suggests that Δ_{CF} does not vary much either in usual CoX₆ systems despite the different coordinating structures. To highlight the uniqueness of the LS tendency in Co²⁺ systems, we have compared the LS-HS energetics of isostructural CoCl₂ and MnCl₂ systems. Following the same idea of Eq. (1), Mn²⁺ (d^5) has $\Delta E = E_{\text{LS}} - E_{\text{HS}} = 6J - 2\Delta_{\text{CF}}$, and so a much larger LS-HS energy difference (by $4J - \Delta_{\text{CF}}$) can be expected. Indeed, as shown in Fig. 1(b), ΔE for MnCl₂ is obtained to be more than 2000 meV without U (3500 meV with $U = 2.0$ eV), which is much larger than that for CoCl₂.

Let us now consider the possible manipulation to make the metastable LS phase stabilized over the HS phase. The easiest way is to apply pressure. When pressure is applied on the system, Δ_{CF} will be increased due to the contraction of Co- X distances, and eventually the HS to LS transition can be realized when Δ_{CF} becomes larger than J . However, as mentioned earlier, the emergence of the Mott physics coming from the change of U and W under pressure can complicate the approach. It is worth noting here that, according to recent theoretical studies [32,33], the effective U value for the d^7 system is independent of the pressure, while that for the d^5 Mott system decreases under pressure. Then we can safely assume constant U in the following pressure studies.

To treat the Co²⁺ system in terms of J versus Δ_{CF} physics, we have to consider two interconnected factors: W and compressibility. In the case of the TM oxides (fluorides), the hybridization between TM-3d and O-2p (F-2p) bands is very strong, and highly dependent on the pressure. Hence, as the pressure increases, W changes much and the resulting resilience of the TM-O bond changes the shapes of the octahedra as well. Thereby, pressure changes not only Δ_{CF} but also W . Moreover, due to the rigidity of the TM-3d and O-2p (F-2p) bonds, the structural transitions occur easily under pressure. So there are overall changes in the octahedral rotation patterns and the connectivity, which makes the system more dependent on the W value.

The compressibility, i.e., the volume change with respect to pressure, should also be taken into account. A system with high compressibility can be a good candidate of the spin-state transition, since Δ_{CF} can be controlled under small pressure without distorting the system or changing the W value. It is known that chlorides usually have better compressibility than oxides and fluorides [34], because the hybridization of d - p bands does not change much upon pressure.

Based on the above criteria, we present CoCl₂ as an ideal model system to study J versus Δ_{CF} physics for the following reasons: (i) The W effect is much reduced due to weaker bonding between Co- d and Cl- p , and accordingly the compressibility is very large. (ii) No structural phase transition occurs up to the spin-state transition pressure [18]. This is in

contrast to CoF_2 , for which the structural transition is easily induced under pressure even below 10 GPa [35]. (iii) Unlike other Co^{2+} systems, the orbital magnetic moment is small ($\sim 10\%$ of the spin magnetic moment), so that the magnetic behavior can be described by the spin magnetic moment only [36]. (iv) The Jahn-Teller distortion is suppressed in the LS phase [18]. This is important because the Jahn-Teller distortion in many half-filled e_g orbital systems makes the situation complicated [37]. (v) Finally, the extensive band calculations are tractable due to its rather simple structure (trigonal space group $R\bar{3}m$).

CoCl_2 contrasts well with CoO , which is one of the most studied Mott insulators governed by U versus W physics. In CoO , strong bonding between Co-3d and O-2p gives resilience to the system, and so the resulting compressibility is small. Consequently, the spin-state transition pressure is as high as 90 GPa, which is about three times higher than that of CoCl_2 . Moreover, several structural transitions exist before reaching the transition pressure [38–42]. Also, the large total magnetic moment of CoO , 3.8–3.98 μ_B , reflects the large orbital magnetic moment of Co^{2+} , which hampers the accurate description of the electronic structure of the system [43–45].

Figure 2(a) provides the FSM calculational results of CoCl_2 for two different volumes, the equilibrium ($V/V_0 = 1.0$) and $V/V_0 = 0.72$. For $V/V_0 = 0.72$, the LS state is stabilized over the HS state with ΔE of ~ 300 meV. The related partial density of states (PDOS) of the Co-3d band for each case is shown

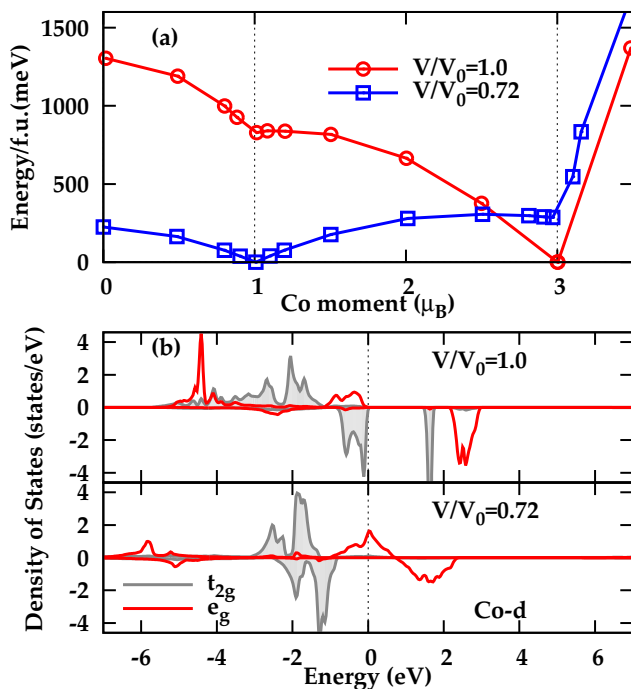


FIG. 2. (Color online) (a) The FSM calculations for CoCl_2 at the equilibrium volume ($V/V_0 = 1.0$) and at the LS stabilized volume ($V/V_0 = 0.72$). (b) PDOS of Co-3d (t_{2g} and e_g) band for each volume. The positive and negative DOSs correspond to majority and minority spin channels, respectively. At the equilibrium volume, the insulating HS state is well-established, while at the LS stabilized volume, the half-metallic LS state is realized. Results are in the GGA + U scheme with $U = 2$ eV.

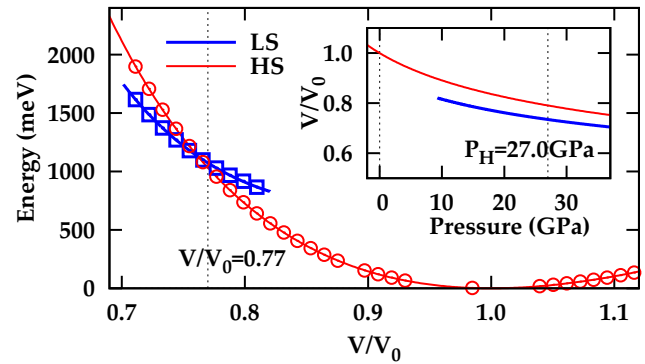


FIG. 3. (Color online) Energy (E) vs volume curve for CoCl_2 shows the spin-state transition at $V/V_0 = 0.77$. Inset: Volume vs pressure curve obtained from enthalpy $H = E + pV$. Abrupt volume collapse can be found at the transition pressure denoted by the vertical dotted line. Results are in the GGA + U with $U = 2$ eV.

in Fig. 2(b). At the equilibrium volume, the HS ($t_{2g}^5 e_g^2$) state with a large band gap is obtained, while for $V/V_0 = 0.72$, the LS ($t_{2g}^6 e_g^1$) metallic state is obtained, which indicates that the spin-state transition is accompanied by the insulator-to-metal transition. Contrary to Mott systems that show highly increased bandwidth upon pressure, the overall bandwidth of Co- d in CoCl_2 does not vary much, which reflects the restricted effect of W in this system [46]. Interestingly, in the LS state, the Fermi level cuts the spin-up e_g band only, so as to produce the half-metallic nature. This point will be discussed more below.

In the case of Mott-type systems, the simple DFT + U (where DFT denotes density functional theory) scheme fails to describe the insulator-to-metal transition. For example, for CoO , the DFT + U approach reproduced the observed pressure-induced HS to LS transition successfully, but failed to manifest the insulator-to-metal transition [42]. The same failure occurred for MnO [47]. Kuneš *et al.* [1] have shown that the dynamical treatment is necessary to explain the spin-state transition in Mott systems. In contrast, in the case of CoCl_2 , U/W physics is not pronounced, and so the description of the insulator-to-metal transition is possible in terms of the DFT + U . The success in the description of CoCl_2 within the DFT + U scheme, in turn, implies that the system is governed by J versus Δ_{CF} physics [46,48].

In Fig. 3, we have shown the energy-volume curves for both HS and LS phases. The spin-state transition is found at around $V/V_0 = 0.77$ for $U = 2$ eV. In the inset, the volume versus pressure curve is also shown. Transition pressure (P_H) obtained from the Maxwell construction is marked with a vertical dotted line at 27.0 GPa, which fits well with the experimental value of 30 GPa [18]. The transition pressure is known to increase with U [42,47], and we can find the same tendency for CoCl_2 too (see Table I). An appropriate U value can be determined by comparison with the experiment [18], which agrees with our calculation on the occurrence of the insulator-to-metal transition.

It is noteworthy that, as in the case of Mott-type transition in MnO and Fe_2O_3 , an abrupt volume collapse as large as 7.2% occurs at the position of the spin-state transition (see the inset in Fig. 3) [49–51]. According to Pasternak *et al.* [50], the Mott

TABLE I. Critical volume and pressure at the spin-state transition in CoCl_2 for each U value. P_E is obtained from the internal energy crossover, and P_H is obtained from the Maxwell construction of enthalpy for the HS and LS states.

U (eV)	0	1.0	2.0	3.0
V/V_0	0.87	0.81	0.77	0.73
P_E (GPa)	13.4	22.1	33.3	41.6
P_H (GPa)	9.7	16.2	27.0	38.5

transition does not lead to a volume collapse at the pressure-driven transition. The volume collapse manifested in CoCl_2 can be a good complementary example suggesting the spin-state transition as a source of volume collapse upon pressure.

The transition behavior of CoCl_2 is totally different from that of Mott-type systems, such as CoO and MnO . While the latter show continuous transition with the change of population in e_g and t_{2g} orbitals for some pressure range [1,38,52,53], the former shows a sudden switch from HS to LS phase due to its intrinsic metastable character of Co^{2+} [Fig. 2(a)]. Also, the transition character in Co^{2+} systems is totally different from that in Co^{3+} systems, for which the thermal excitation promotes the population change of e_g and t_{2g} bands [8,10].

The evolution of the magnetic moment as a function of volume is described in Fig. 4. One can find the hysteresis behavior as the HS phase is turned to the LS phase and vice versa between $V/V_0 = 0.75$ and 0.80. Since many HS Co^{2+} systems have sizable orbital moment due to incomplete quenching, the total moment change in some systems can be larger than $2\mu_B$ at the spin-state transition.

In CoCl_2 , as the spin-state changes from HS to LS, the magnetic structure is also found to change from antiferromagnetic (AFM) to ferromagnetic (FM). The HS AFM structure is described as FM layers coupled antiferromagnetically along the hexagonal c axis [30,36]. We compared total energies of AFM and FM CoCl_2 for different volumes and found that, at $V/V_0 = 1.0$, the AFM state is favored by 5 meV/f.u., while at $V/V_0 = 0.72$, the FM state is favored by 15 meV/f.u.

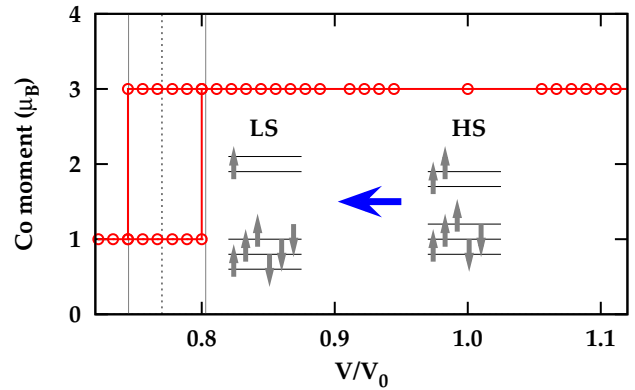


FIG. 4. (Color online) Spin magnetic moment vs volume curve for CoCl_2 shows hysteresis behavior between HS and LS states. The vertical dotted line corresponds to $V/V_0 = 0.77$, corresponding to the internal energy crossover volume. Schematic diagrams of corresponding HS and LS states are also shown.

Moreover, as shown in Fig. 2(b), the half-metallic state emerges in the FM state at $V/V_0 = 0.72$, which suggests that the double exchange mechanism becomes prevailing due to the conducting e_g electrons in the metallic LS phase.

In conclusion, we have confirmed the generality of the metastable LS state in the octahedrally coordinated Co^{2+} systems. For CoCl_2 , as a prototypical Co^{2+} system, we have demonstrated the pressure-induced spin-state transition, which is governed by J versus Δ_{CF} physics. Due to its high compressibility, Δ_{CF} easily overturns J at around 27 GPa, and the first-order spin-state transition occurs from HS to LS with substantial volume collapse in conjunction with the insulator-to-metal and AFM to half-metallic FM transitions. Since the Mott physics can be excluded, we can argue that the spin-state transition and relevant behaviors found in CoCl_2 are general features of a system with J versus Δ_{CF} physics.

We would like to thank H. C. Choi and G. Lee for helpful discussions. This work was supported by the NRF (Grant No. 2009-0079947), and by the KISTI supercomputing center (Grant No. KSC-2012-C2-27).

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