
**MAGNETISM
AND FERROELECTRICITY**

Electronic Structure and Magnetic States of Crystalline and Fullerene-Like Forms of Nickel Dichloride NiCl₂

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Abstract—The electronic structure and magnetic properties of the crystalline and fullerene-like forms of nickel dichloride NiCl₂ are investigated in the framework of the local spin density functional theory. It is demonstrated that the band gap can be reproduced in the energy band spectrum of the NiCl₂ compound with inclusion of the magnetic ordering in the calculation of the band structure. The metamagnetic nature of the NiCl₂ dichloride (i.e., the transition from an antiferromagnetic phase to a ferromagnetic phase in a weak magnetic field) is explained in terms of a small difference (0.025 eV/cell) between the total energies of the ferromagnetic and antiferromagnetic phases. Polyhedral three-shell nanoparticles of the NiCl₂ compound exhibit magnetic properties (the magnetic moment of nickel lies in the range 2.0–2.3 μ_B). For isostructural nanoparticles of the FeCl₂ dichloride, the magnetic moment of iron is larger and falls in the range 4.2–4.5 μ_B, whereas nanoparticles of the CdCl₂ dichloride are found to be nonmagnetic. The results of analyzing the interatomic interactions indicate that the composition of fullerene-like nanoparticles of the dichlorides under investigation can deviate from the 1 : 2 stoichiometric composition. © 2005 Pleiades Publishing, Inc.

1. INTRODUCTION

Among the magnetic materials suitable for a wide range of practical applications, quasi-two-dimensional metamagnetic systems are of particular interest. The best known representatives of these systems are nickel dichloride NiCl₂ and isostructural *d* metal dihalides of the CdCl₂ type. In the ground state, the NiCl₂ dichloride is an antiferromagnetic material. The NiCl₂ compound in the antiferromagnetic phase has a structure consisting of nickel ferromagnetic layers in which the adjacent layers are antiferromagnetically ordered [1, 2]. The NiCl₂ dichloride undergoes a transition from the antiferromagnetic phase to the ferromagnetic phase in weak magnetic fields.

The mechanism responsible for the formation of a band gap in the energy band spectrum of the NiCl₂ dichloride and a number of other crystalline nickel-containing compounds has been a matter of great discussion between different groups of researchers [3]. In particular, the one-electron spin-restricted calculations performed by Ackerman *et al.* [4] predicted that the NiCl₂ dichloride should possess metallic conductivity. However, Ronda *et al.* [3] carried out experimental investigations of the photoconductivity in nickel dichloride and revealed that the energy band spectrum of this compound is characterized by a band gap of ~4.6 eV. Antoci and Minich [5] and Zaanen *et al.* [6] assumed that the formation of a band gap in the band spectrum of nickel dichloride can be caused by transitions from a Ni 3*d*–Cl 3*p* occupied band to a Ni *d* empty energy band rather than by transitions between *d*–*d*

states of nickel; i.e., the band gap in the band spectrum of this compound is associated with charge-transfer transitions and is not a Mott–Hubbard gap, in contrast to the case with nickel oxide NiO. The question regarding the role played by magnetism in the formation of a band gap in the energy band spectrum of the NiCl₂ dichloride remains open.

Quite recently, Hacoheh *et al.* [7] synthesized unique quasi-one-dimensional and quasi-zero-dimensional nanostructures of nickel dichloride (namely, nanotubes and polyhedral fullerene-like nanoparticles, respectively) through reactive laser ablation [7]. Moreover, Hacoheh *et al.* [8] and Popovitz-Biro *et al.* [9] prepared a number of fullerene-like nanoparticles from related metal dihalides, such as CdI₂, CdCl₂, and FeCl₂. However, there are no reliable data on the electronic and magnetic properties of these low-dimensional systems.

In this work, the electronic structure and magnetic states of the crystalline (two-dimensional) and fullerene-like (zero-dimensional) forms of the NiCl₂ dichloride were thoroughly investigated within the local spin density functional theory formalism for the first time. Moreover, we examined the magnetic properties of FeCl₂ and CdCl₂ fullerene-like nanoparticles.

2. COMPUTATIONAL TECHNIQUE, RESULTS, AND DISCUSSION

Nickel dichloride NiCl₂ has a layered structure (space group $R\bar{3}m$) consisting of molecular layers,

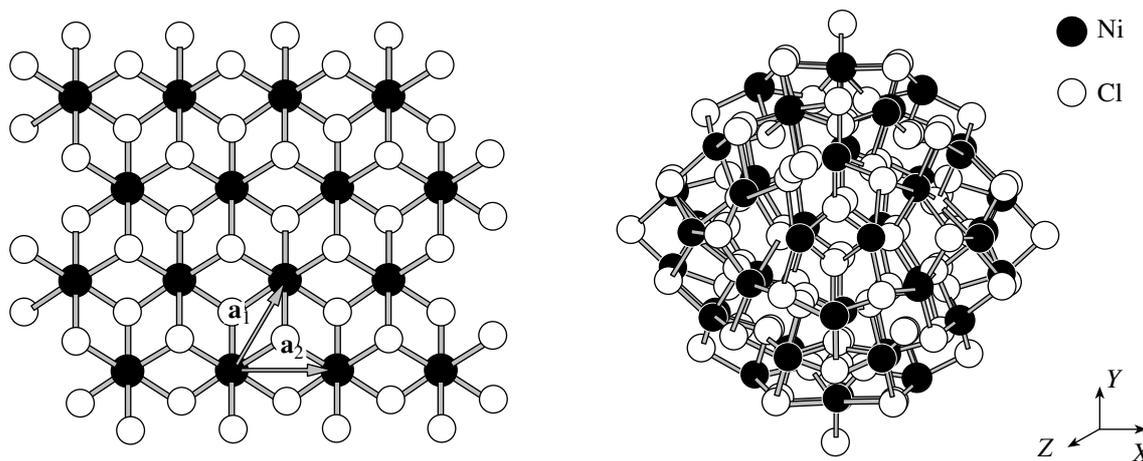


Fig. 1. Atomic structures of a fragment of the NiCl_2 molecular layer (\mathbf{a}_1 and \mathbf{a}_2 are translational vectors) and a polyhedral (fullerene-like) nanoparticle of the composition $(\text{NiCl}_2)_{48}$.

each composed of three Cl–Ni–Cl atomic networks (Fig. 1). The band structure of the NiCl_2 crystal was calculated using the linearized muffin-tin orbital method [10] for three phases, namely, the nonmagnetic, ferromagnetic, and real antiferromagnetic phases. The antiferromagnetic phase has a structure composed of nickel

ferromagnetic layers in which the adjacent layers are antiferromagnetically ordered [1, 2]. In the nonmagnetic phase of the NiCl_2 compound, the Fermi level E_F is located at a maximum of the electron density of nickel d states. Owing to the ferromagnetic ordering, the total energy of the system decreases by ~ 0.31 eV and the energy band spectrum is characterized by a band gap of ~ 0.35 eV (Fig. 2). Thus, the comparison of the results obtained for the nonmagnetic and ferromagnetic phases of the NiCl_2 dichloride shows that the band gap can be reproduced in the energy band spectrum of this compound with inclusion of the in-plane magnetic ordering in the band structure calculation performed in the framework of the local spin density functional theory.

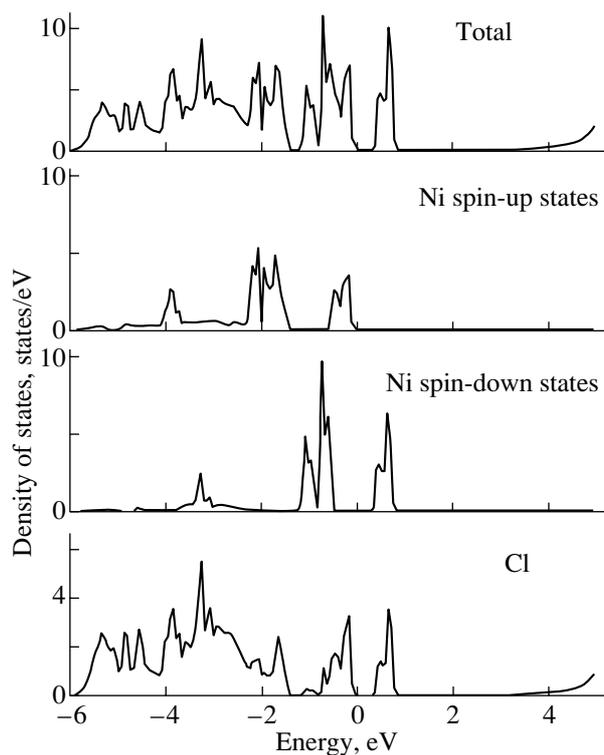


Fig. 2. Total and partial densities of states of the NiCl_2 ferromagnetic phase according to the linearized muffin-tin orbital calculations.

In the NiCl_2 compound, Ni^{2+} ions have a $3d^8$ configuration in which six electrons occupy the t_{2g} bands and two electrons are localized in the e_g bands. In the ferromagnetic phase of the NiCl_2 compound, electrons occupy the t_{2g} spin-up states, the e_g spin-up states, and the t_{2g} spin-down states. The top of the valence band is formed by the e_g bands overlapping with the Cl $3p$ states; i.e., the formation of the band gap is associated with transitions between the e_g^\uparrow hybridized states and the e_g^\downarrow unoccupied states (Fig. 2). The magnetic moment of nickel is equal to $1.3 \mu_B$.

The inclusion of the antiferromagnetic ordering between the nickel ferromagnetic layers leads to a lowering of the e_g^\uparrow occupied band and an increase in the band gap to 0.42 eV. It should be particularly emphasized that the total energy of the antiferromagnetic phase is 0.025 eV lower than the total energy of the ferromagnetic phase. In this case, the band structures of the antiferromagnetic and ferromagnetic phases differ insignificantly. Therefore, the electronic properties of

the NiCl_2 dichloride are only slightly affected by the antiferromagnetic ordering and the metamagnetic nature of this compound (i.e., the transition from the antiferromagnetic phase to the ferromagnetic phase in a weak magnetic field) can be explained in terms of the very small difference between the total energies of the ferromagnetic and antiferromagnetic phases.

Atomic models of the low-dimensional structures of the NiCl_2 compound were constructed on the basis of a Cl–Ni–Cl molecular layer. This layer can be described by the primitive translational vectors \mathbf{a}_1 and \mathbf{a}_2 (Fig. 1). Models of the chiral and achiral nanotubes were obtained by rolling “ribbons” cut from a layer of width $|c| = na_1 + ma_2$ [7, 11]. Fullerene-like nanoparticles were simulated with the use of NiCl_2 layer fragments serving as nanoparticle faces. In order to provide alternation of the Ni–Cl bonds, vertices of these fullerene-like nanoparticles, unlike carbon fullerenes, must be occupied by even numbers of atoms. With due regard for this requirement, it is possible to simulate only one type of polyhedral particles in which the face walls are built of NiCl_6 octahedra shared by edges and each vertex is formed by two octahedra shared by faces (Fig. 1). In order to ensure the stoichiometric composition NiCl_2 , it is necessary to remove two chlorine atoms, for example, from two vertices of the fullerene-like nanoparticles (Fig. 1). Such fullerenes of the stoichiometric composition NiCl_2 are three-shell nanoparticles of the cage type in which the outer and inner shells are composed of chlorine atoms and the middle shell consists of nickel atoms. These nanoparticles have octahedral morphology, which was experimentally observed by Hachen *et al.* [7].

The electronic and magnetic properties of NiCl_2 , FeCl_2 , and CdCl_2 fullerene-like nanoparticles were investigated by using the example of polyhedral nanoparticles of the composition $(\text{MCl}_2)_{48}$. The particle geometry was optimized by the MM+ molecular mechanics method with allowance made for dipole interactions. The calculations were performed using the spin-polarized discrete-variational method [12]. The model densities of states are presented in Fig. 3. The Cl 3*p* states are located in the energy range 8–2 eV below the Fermi level E_F . The near-Fermi states predominantly involve the Ni 3*d* orbitals. Fullerene-like nanoparticles of the composition $(\text{NiCl}_2)_{48}$ are characterized by a metal-like band spectrum. A similar band spectrum is obtained for $(\text{FeCl}_2)_{48}$ nanoparticles. For $(\text{CdCl}_2)_{48}$ nanoparticles, the upper valence band is predominantly formed by the Cl 3*p* states and the lowest free energy states are of the mixed Cd 5*s*–Cl 3*p* type. The band gap is approximately equal to 0.5 eV. The atomic magnetic moments of the $(\text{NiCl}_2)_{48}$, $(\text{FeCl}_2)_{48}$, and $(\text{CdCl}_2)_{48}$ fullerene-like nanoparticles were calculated from the populations of the atomic spin orbitals. According to these calculations, the atomic magnetic moments are equal to 2.0–2.3 μ_B for the $(\text{NiCl}_2)_{48}$ nanoparticles and 4.2–4.5 μ_B for the $(\text{FeCl}_2)_{48}$ nanoparticles. The $(\text{CdCl}_2)_{48}$ nanoparticles are found to be nonmagnetic.

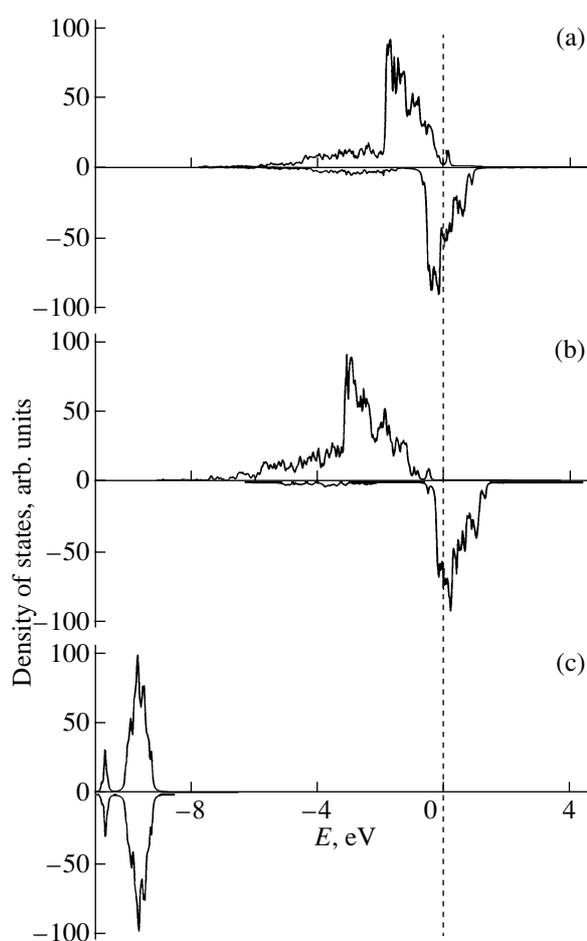


Fig. 3. Model densities of *d* states of metal atoms in (a) $(\text{NiCl}_2)_{48}$, (b) $(\text{FeCl}_2)_{48}$, and (c) $(\text{CdCl}_2)_{48}$ fullerene-like nanoparticles according to the spin-polarized discrete-variational calculations. The vertical line indicates the edge of the occupied band.

The calculations of the overlap integrals and the effective atomic charges Q demonstrated that the Coulomb interactions play a dominant role in the stabilization of the $(\text{NiCl}_2)_{48}$ and $(\text{FeCl}_2)_{48}$ fullerene-like nanoparticles, whereas the covalent component of the bond is small (the overlap integral is less than 0.1 e). The degree of ionicity of the bond is estimated from the 2 Pauling formula and is approximately equal to 75%. The atomic charges of the metallic shell of the nanoparticles fall in the range $+(0.33\text{--}0.41)$ for nickel and in the range $+(0.35\text{--}0.46)$ for iron. Two groups of atoms can be clearly distinguished among the nonequivalent chlorine atoms involved in the outer and inner shells of the fullerene-like nanoparticles. For atoms of the first group, the effective atomic charges Q lie in the range $-(0.19\text{--}0.36)$ for the $(\text{NiCl}_2)_{48}$ nanoparticles and in the range $-(0.25\text{--}0.30)$ for the $(\text{FeCl}_2)_{48}$ nanoparticles. For atoms of the second group, the effective charges Q are considerably smaller and equal to ~ -0.07 for the $(\text{NiCl}_2)_{48}$ nanoparticles and $-(0.01\text{--}0.10)$ for the

(FeCl₂)₄₈ nanoparticles. This implies that chlorine atoms of the latter group are weakly bonded to metals atoms and can easily leave the nanoparticle cage. This group contains 36 chlorine atoms located in the inner shell of the nanoparticle. Therefore, the 1 : 2 stoichiometric composition of the fullerene-like nanoparticle can change to 1 : 1.25. This ratio is in good agreement with the results obtained in [7–9], according to which the composition of the dichloride fullerene-like nanoparticles synthesized is characterized by a ratio of 1 : 1.2 (or less).

3. CONCLUSIONS

Thus, the electronic structure and magnetic states of the crystalline and fullerene-like forms of the NiCl₂ dichloride were investigated using the linearized muffin-tin orbital and discrete-variational methods in the framework of the local spin density functional theory. It was demonstrated that the band gap can be reproduced in the energy band spectrum of the NiCl₂ crystal with inclusion of the magnetic ordering in the calculation of the band structure. The calculations of the total energies for three phases, namely, the nonmagnetic, ferromagnetic, and antiferromagnetic phases, showed that the antiferromagnetic phase is more stable. The metamagnetic nature of the NiCl₂ dichloride and the transition from the antiferromagnetic phase to the ferromagnetic phase in a weak magnetic field were explained in terms of the small difference between the total energies of the ferromagnetic and antiferromagnetic phases.

It was established that NiCl₂ polyhedral three-shell (fullerene-like) nanoparticles possess magnetic properties (the magnetic moment of nickel is equal to 2.0–2.3 μ_B). For isostructural fullerene-like nanoparticles of the FeCl₂ dichloride, the magnetic moment of iron is larger and falls in the range 4.2–4.5 μ_B , whereas nanoparticles of the CdCl₂ dichloride are found to be nonmagnetic. The results of analyzing the interatomic interactions indicate that the composition of dichloride fullerene-

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SPELL: 1. achiral, 2. ionicity