Mapping of the DFT Spin Configuration Energies of Cr8Cd Molecular Ring onto the Energy Structure of Falicov–Kimball Model

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A comprehensive study of electronic and magnetic properties of a recently synthesized nonametalic chromium-based heteronuclear molecule $Cr_8CdF_9(O_2C - C(CH_3)_3)_{18}$ is presented, using DFT and Falicov–Kimball (FK) model approach. The magnetic moments are calculated and the spin charge density map is discussed. The exchange coupling parameters between transition metals ions are extracted, taking into account all the nonequivalent spin configurations. It is demonstrated that the energies of the spin configurations can be reproduced by the FK model with a set of parameters consistent with that for the parent Cr8 molecule. For molecular ring considered, the ground state corresponds to the antiferromagnetic configuration and the ferromagnetic configuration yields the highest energy.

1. Introduction

Magnetic molecules have been an object of continued study ever since they were discovered [1]. Molecular rings are a subgroup of those materials that are ideal for investigating electric and magnetic properties of spin coupled systems. These properties depend mostly on transition metals embedded in the molecule. Due to their small size they need to be treated in a quantum manner, yet they are to big for exact calculations.

These molecules exhibit many fascinating physical phenomena such as magnetic memory effect, resonant tunnelling of magnetization or hysteresis step curves of magnetization. Furthermore they are considered to be useful in new generation of high density data storage devices or quantum computing.

A class of molecular rings that is currently being extensively researched uses chromium for its paramagnetic canters [2, 3]. In this paper we show results for a $Cr_8CdF_9(O_2C - C(CH_3)_3)_{18}$ (Cr8Cd in short) or to be more exact for $Cr_8CdF_9(O_2C - H)_{18}$. In our calculations we use a molecule in which each pivalic group $C(CH_3)_3$ is substituted by a single H atom [4–6], so that the ring is made up out of eight Cr atoms and a single Cd atom. They are connected to each other via two $-O - CH - O-$ bridges and a single $-F-$ bridge and are almost in one plane. The molecule is presented in Fig. 1.

Earlier results for the Cr8 family [6] and Cr9 molecule [7] show that the Falicov–Kimball model (FKM) approach can lead to energy spectrum very similar to

the one obtained from DFT calculations for all the nonequivalent spin confgurations. Here we would like to show that FKM can also be used for determination of the energy spectrum of the heteronuclear Cr8Cd ring molecule.
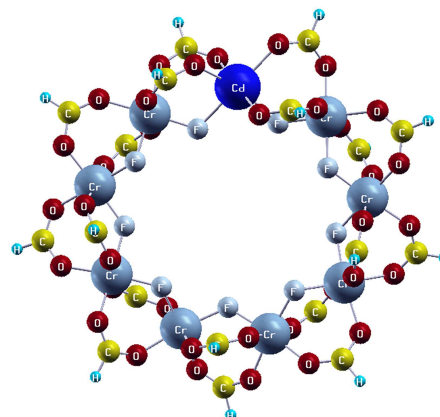

Fig. 1. The structure of the Cr8Cd molecule with hydrogen atoms in place of pivalic groups.

2. Results and discussion

The main calculations were carried out for all nonequivalent spin configurations with $s = \pm 3/2$ for Cr ions and $s = 0$ for Cd ion using Siesta package [8]. A custom pseudopotential for Cr [9] was used. The ground state for Cr8Cd molecule is a antiferromagnetic (AFM) one. The spin density plot for AFM state is shown in Fig. 2. In this state the total magnetic moment $m = 3\mu_B$. A significant spin polarization of the charge density is found only

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close to the transition metal atoms, confirming a localized picture of the Cr magnetic moments [10]. Magnetic moments found using Mulliken analysis have the values 0 for the Cd ion and $\pm(2.86-2.93)\mu_\mathrm{B}$ for all Cr ions. The values of magnetic moments for the remaining atoms are close to 0. Calculated values are shown in Table I.
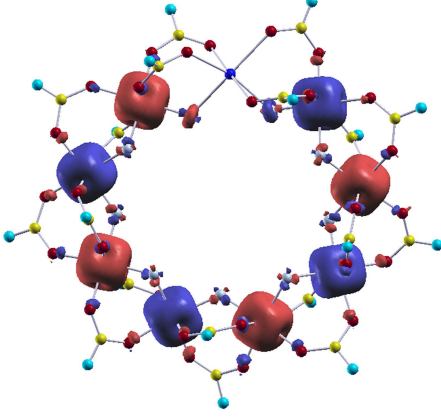

Fig. 2. Spin density plot for Cr8Cd molecule in the ground AFM state. Red (blue) shades are positive (negative) isosurfaces for the value ± 0.01 e/Bohr^3.

TABLE I

Magnetic moments (MM) in units of μ_B found using Mulliken analysis for Cr and Cd ions for Cr8Cd molecule in the ground AFM state. The numeration of ions is as shown in Fig. 3.

Cd(1)	Cr(2)	Cr(3)	Cr(4)	Cr(5)	Cr(6)	Cr(7)	Cr(8)	Cr(9)
−0.001	+2.90	−2.89	+2.89	−2.90	+2.93	−2.91	+2.86	−2.90

Coupling constants were also estimated using the standard broken symmetry approach [11]. Fig. 3. shows different models of couplings between Cr ions.

TABLE II

Exchange interaction parameter for different schemes of interaction between Cr atoms shown in Fig. 3. All values in units of meV.

model	J_1	J_2	J_3	J_4
(a)	4.3			
(b)	4.2	4.8		
(c)	4.0	4.8	4.4	
(d)	4.2	4.8		0.1

We find that for Cr ions depending on the particular schematic the nearest-neighbor (NN) coupling constant J_1 varies from 4.0 meV to 4.3 meV. The J_2 constant is stable with the value 4.8 meV [3]. The next-nearest-neighbor (NNN) interaction is neglectable. As to be expected, these values are overestimated in comparison to the experimental value of $J_\mathrm{exp} = 1.3$ meV [12]. Exchange interaction parameters are shown in Table II.
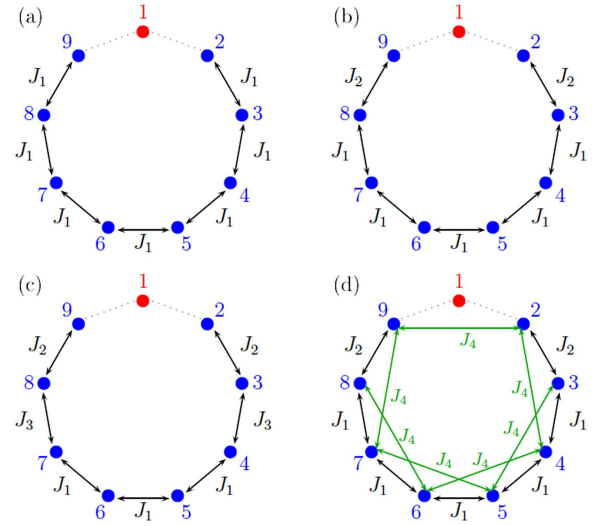

Fig. 3. Different schematic representations of nearest neighbor exchange coupling between the ions for Cr8Cd molecule. Blue dots represent Cr(III) ions and red dot represent Cd(II) ions.

Another approach for study of molecular magnetic rings is the Falicov–Kimball model (FKM) [13] extended by Hund coupling [14, 15] between spins of electrons and ions [16]. The Hamiltonian of this model is

$$H = \sum_{\langle m,n \rangle} \sum_{\sigma=\uparrow,\downarrow} t_{mn} d^+_{m,\sigma} d_{n,\sigma}$$
$$+ \sum_m U_m n^d_m n^f_m + \sum_m J^H_m s^Z_m S^Z_m,$$

where $\langle m,n \rangle$ denotes the nearest neighbor sites m and n of the ring, σ is a spin indice, $d^+_{m,\sigma}$ ($d_{n,\sigma}$) is an annihilation (creation) operator of electron, n^d_m (n^f_m) is an occupation number of electron (ion), s^Z_m (S^Z_m) stands for a z-component of spin of electron (ion). The on-site interaction between electron and magnetic ion is represented by two coupling constants: U_m which is the Coulomb-type, and J^H_m which reflects the Hund rule force. The electron hopping amplitude between two adjacent ions is t_{mn}.

In general, the parameters U_m and J^H_m are different for Cr and Cd ions. Usually also t_{mn} takes different values for the pairs of ions Cd-Cr and Cr-Cr. This parametrization is illustrated in Fig. 4.

For 10 itinerant electrons in the system and hopping amplitude between distant Cr ions $t \approx 96$ meV, setting $J = 2t$, $U = 16t$, $U_x = 10t$ and hopping amplitude between Cr and Cd ions $t_x = 1.5t$ and between Cr ions nearest to Cd ion $t_y = 1.02t$ leads to proper representation of the total energies corresponding to different spin arrangements with respect to the antiferromagnetic ground state as shown in Fig. 5. The configurations are aligned according to the increasing value of their energies. The label 1 corresponds to the AFM configuration, whereas that equal 72 to the FM configuration.
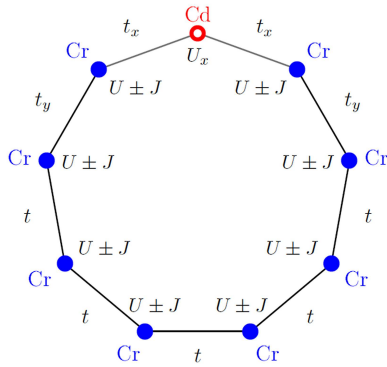
Fig. 4.   Schematic representation of the Cr8Cd molecular ring studied within the Falicov–Kimball model. Full circles denote magnetic Cr ions and the open circle denote Cd ion. The symbols t, t_x, t_y, U, U_x, J refer to the FK model parameters.
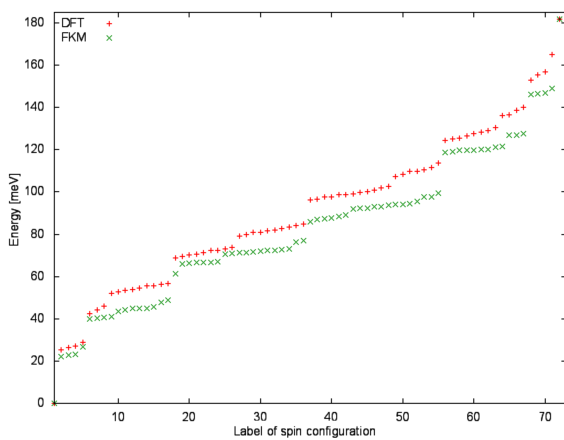

Fig. 5.   Energies of Cr8Cd ring for all the nonequivalent spin configurations of the ions, referred to the ground state, found within the DFT and FKM approach.

Let us notice that the chosen values for on-site Coulomb interaction parameters and for the hopping amplitudes coincide with those for Cr8 molecule [6] and are comparable to the values provided in the literature for the Hubbard model [17].

3. Conclusions

We have carried out the systematic SIESTA-based DFT calculations for the Cr8Cd molecule. We have shown that exchange couplings are in quantitative agreement with other DFT theoretical investigations for the Cr8 family and Cr9 molecule [6, 17]. Additionally, we have shown that the approach based on the Falicov–Kimball model is capable of providing accurate energy levels for different spin configurations of molecular nanomagnet Cr8Cd for the parameters which coincide with those describing Cr8.

References

[1] D. Gatteschi, R. Sessoli, J. Villain, *Molecular nanomagnets*, Oxford University Press, New York 2006.

[2] M.L. Baker, T. Guidi, S. Carretta, J. Ollivier, H. Mutka, H.U. Güdel, G.A. Timco, E.J.L. McInnes, G. Amoretti, R.E.P. Winpenny, P. Santini, *Nature Physics* **8**, 906 (2012).

[3] M.L. Baker, G.A. Timco, S. Piligkos, J.S. Mathieson, H. Mutka, F. Tuna, P. Kozłowski, Michał Antkowiak, T. Guidi, T. Gupta, H. Rath, R.J. Woolfson, G. Kamieniarz, R.G. Pritchard, H. Weihe, L. Cronin, G. Rajaraman, D. Collison, E.J.L. McInnes, R.E.P. Winpenny, *Proc. Nat. Acad. Sci.* **109**, 19113 (2012).

[4] V. Bellini, A. Olivieri, F. Manghi, *Phys. Rev. B* **73**, 184431 (2006).

[5] T. Ślusarski, B. Brzostowski, D. Tomecka, G. Kamieniarz, *J. Nanosci. Nanotechnol.* **11**, 9080 (2011).

[6] B. Brzostowski, R. Lemański, T. Ślusarski, D. Tomecka, G. Kamieniarz, *J. Nanopart. Res.* **15**, 1528 (2013).

[7] B. Brzostowski, M. Wojciechowski, R. Lemański, G. Kamieniarz, G.A. Timco, F. Tuna, R.E.P. Winpenny, *Acta Phys. Pol. A.* **126**, 270 (2014).

[8] J. M. Soler, E. Artacho, J. D. Gale, A. GarcÅa, J. Junquera, P. Ordejón, D. Sánchez-Portal, *J. Phys.: Condens. Matter* **14**, 2745 (2002).

[9] B. Brzostowski, T. Ślusarski, G. Kamieniarz, *Acta Phys. Pol. A.* **121**, 1115 (2012).

[10] M. Antkowiak, P. Kozłowski, G. Kamieniarz, G.A. Timco, F. Tuna, R.E.P. Winpenny, *Phys. Rev. B* **87**, 184430 (2013).

[11] E. Ruiz, J. Cano, S. Alvarez, P. Alemany, *J. Comp. Chem.* **20**, 1391 (1999).

[12] A. Ghirri, A. Candini, M. Evangelisti, M. Affronte, S. Carretta, P. Santini, G. Amoretti, R.S.G. Davies, G. Timco, R.E.P. Winpenny, *Phys. Rev. B* **76**, 214405 (2007).

[13] L.M. Falicov, J.C. Kimball, *Phys. Rev. Lett.* **22**, 997 (1969).

[14] J. Hubbard, *Proc. Roy. Soc. (London) A* **276**, 238 (1963).

[15] M.C. Gutzwiller, *Phys. Rev. Lett.* **10**, 159 (1963).

[16] R. Lemański, *Phys. Rev. B* **71**, 035107 (2005).

[17] P. Werner, E. Gull, A.J. Millis, *Phys. Rev. B* **79**, 115119 (2009).