

## Magnetic trimer on non-magnetic substrate: From frustration towards non-collinearity

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(received 12 March 1999; accepted in final form 5 July 1999)

PACS. 36.40Cg – Electronic and magnetic properties of clusters.

PACS. 71.24+q – Electronic structure of clusters and nanoparticles.

PACS. 75.30Pd – Surface magnetism.

**Abstract.** – We present the very first non-collinear magnetic structure calculations of supported metallic 3d triangular trimers. Within the vector Anderson model, in dependence on the ratio between hopping parameters in the trimer the ground state can be collinear or non-collinear. Calculations performed for the Cr and Fe trimers show that the modulus of the magnetic moments per atom are enhanced relatively to bulk value. The dependence, *vs.* hopping integrals, of the angles between the magnetic moments is different when going from Cr to Fe although these angles are equal to 120 degrees in the ground state of the equilateral triangle.

Magnetic nanostructures on non-magnetic substrate has attracted recently large attention due to their novel and unusual properties important for the fundamental theory of magnetism as well as for the applications in the new electronic devices. Small magnetic clusters consisting of a few atoms have special interest because firstly, they are the building blocks for epitaxial growth and secondly, they demonstrate very interesting behaviour which can be driven by changing the external conditions such as temperature or magnetic field. Such phenomena cannot be observed either for individual supported atoms due to the simplicity of the system or for the large (on atomic scale) objects like islands or monolayers due to the statistical averaging. The complex magnetic behaviour of small clusters is usually connected with the competition of several interactions and with the existence of several metastable states close in energy. The ground state can therefore be easily changed by external action and this could lead to the switching between different states, which give large modification to the cluster's characteristics as, for example, huge increase of the total magnetic moment.

Recently, Stepanyuk *et al.* [1] within *ab initio* KKR Green's function method have obtained four metastable collinear states with essentially different magnetic moments for 3d trimer- and

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tetramer-supported clusters. Only linear chains were considered in the case of trimers, so that non-collinear state was postulated to be unlikely and was therefore not considered. However, Oda *et al.* [2] using unconstrained local spin-density calculations together with the *ab initio* molecular dynamics method found non-collinear magnetic structure even for free Fe<sub>3</sub> linear chains. In the case of supported triangular clusters non-collinear structure should be equally present.

The conclusion about jump-like transitions between metastable states [1] should be essentially modified if we took into account the possibility of non-collinear state. Such transitions can be observable only if appropriate collinear metastable states give local minimum of the energy as a function of angle between the moments. In this case self-consistent calculations performed for different angles in the non-collinear model will give the potential barrier. If collinear states do not correspond to the local minimum, then transitions between metastable collinear states cannot happen and it is therefore necessary to investigate the behaviour of the trimer's energy around local minima in non-collinear configurations.

Recent scanning tunneling microscopy measurements [3] have shown that, after annealing in Cr/Pt(111) system, Cr atoms at the surface self-organise in superstructure (10 atoms) with threefold symmetry. Magnetic ordering on this (111) substrate has similarity with ordering in the simple magnetic equilateral triangular trimer. From another point of view, *ab initio* calculations in a collinear model of free Cr [4] and V [5] trimers lead to an isosceles triangular structure, with lower energy than for the equilateral triangle. Non-collinear magnetic ordering in small free standing Cr clusters was recently reported by C. Kohl and G. Bertsch [6]. The coupling to the electronic degrees of freedom was treated with relativistic non-local pseudopotentials and the ionic structure was optimised by Monte Carlo techniques. For the Cr trimer ground state was detected also as isosceles triangle. They found that non-collinear spins induce only very small changes in the cluster's geometry relatively to the collinear model.

For supported clusters the interatomic distance is mainly determined by the lattice constant of the substrate. Influence of the non-collinear structure on the interatomic bond's length in this case has to be even less than for the free standing clusters. However, dependence of the angle between the moments on the trimer's geometry is a non-trivial problem which was so far not considered in the literature.

In this letter we report the results of non-collinear magnetic structure calculations for supported isosceles triangular trimers within the model Hamiltonian approach. We used the real space recursion method for the Anderson model in the mean-field approximation. This model is an extension of a previous scheme [7] devoted to non-collinear magnetism in bcc metals in the bulk and at the interface. In summary, non-collinearity leads to the appearance of additional on-site hoppings with inversion of the spin projection apart from intersites hopping without spin inversion. The equations for *d*-electron Green functions  $G_{ij}^{\alpha\beta}$  have the following form:

$$(\omega - E_i^\alpha)G_{ij}^{\alpha\beta}(\omega) - \sum_{k\gamma} V_{ik}^{\alpha\gamma} G_{kj}^{\gamma\beta}(\omega) = \delta^{\alpha\beta} \delta_{ij}.$$

Here lower and upper indices enumerate, respectively, atoms (1, 2, 3) in the trimer and spin projections (+, -),  $\delta$  is the Kronecker symbol.  $E_i^\alpha$  is the energy of the electron at site *i* with spin projection  $\alpha$  and the hopping parameters  $V_{ij}^{\alpha\beta}$  are expressed in terms of the *d*-electron number  $N_i$ , modulus of the magnetic moment  $M_i$ , and the angle  $\theta_i$  between the moments and quantisation axis (in what follows all the moments are supposed to be in plane):

$$E_i^\pm = E_{0i} + \frac{U_i N_i}{2} \mp \frac{U_i M_i}{2} \cos \theta_i, \quad V_{ij}^{\alpha\beta} = (\delta^{\alpha\beta} - 1) \delta_{ij} \frac{U_i M_i}{2} \sin \theta_i + (1 - \delta_{ij}) \delta^{\alpha\beta} v(\mathbf{r}_i, \mathbf{r}_j).$$

The spin-independent part of the energy  $E_{0i}$ , will be counted later on from the Fermi level. the Coulomb integral  $U_i$  and the hopping integral for transition without spin inversion  $v(\mathbf{r}_i, \mathbf{r}_j)$  are assumed to be the parameters of the model.  $v(\mathbf{r}_i, \mathbf{r}_j)$  besides direct hopping between sites  $i$  and  $j$  contains the contribution from the transitions through the conductivity band of the substrate. In general, it depends on the distance between atoms in the trimer as well as on the position of the trimer on the substrate. We connect the value of this parameter mainly with the lengths of the bonds  $v(\mathbf{r}_i, \mathbf{r}_j) = v(|\mathbf{r}_i - \mathbf{r}_j|) \equiv v_{ij}$ : the bigger  $v_{ij}$  the smaller the distance between atoms in the trimer. The  $s$ - $d$  hybridisation leads also to the appearance of the finite width  $\Gamma$  for the  $d$ -states so that in what follows all the energies will be measured in  $\Gamma$ -units. For the atoms of the trimers at distance close to the lattice parameter of the substrate  $v_{ij}$  and  $\Gamma$  have the same order of magnitude.

The magnetic moment  $M_i$  and the number of  $d$ -electrons  $N_i$  on every atom of the trimer is expressed through the imaginary part of  $G_{ij}^{\alpha\beta}$ . The expression for  $M_i$  contains in general the non-diagonal spin matrix elements of the Green function. The dimensionless parameters of the model  $E_{0i}/\Gamma$  and  $U_i/\Gamma$  were chosen so as to reproduce the bulk number of  $d$ -electrons and magnetic moments in bcc ferromagnetic (FM) Fe and antiferromagnetic (AF) Cr [7]. Calculations were performed for the set of hopping integrals  $v_1 \equiv v_{12}/\Gamma = v_{13}/\Gamma$  and  $v_2 \equiv v_{23}/\Gamma$  that corresponds to the isosceles triangular structure.

The quantisation axis is taken along the magnetic moment localised on the first trimer's atom. In this case only two angles  $\theta_2$  and  $\theta_3$  determine the direction of all magnetic moments. These angles were changed from 0 to  $2\pi$  with step  $\pi/100$ . In dependence on the magnitude of the hopping integrals a self-consistent solution exists for different sets of angles  $\theta_2, \theta_3$ . Hopping integrals determine the interaction between electrons localised on different atoms. In the case of non-interacting atoms solutions for every value of  $\theta_2$  and  $\theta_3$  exist and have the same energy. With the increase of the interatomic interactions only some of the angles lead to self-consistent solutions whose energies depend on the mutual moment's orientation.

Calculations show that the energy as a function of the angles  $\theta_2$  and  $\theta_3$  for given  $v_1$  and  $v_2$  have two minima which can be parametrized by the angle  $\theta_0$ :  $\theta_2 = \theta_0$ ;  $\theta_3 = 2\pi - \theta_0$  and  $\theta_3 = \theta_0$ ;  $\theta_2 = 2\pi - \theta_0$ . The modulus of the moments on atoms 2 and 3 of the trimer are found equal at these minima. So, both solutions correspond to the same physical state. Dependences of the angle  $\theta_0$  vs.  $v_1$  for  $v_2 = 0.9$  (circles) and  $v_2 = 1.3$  (triangles) are shown on fig. 1. For  $v_1$  close to 0, atoms 2 and 3 form a dimer which interacts weakly with the atom 1. The Fe trimer moments on the atoms 2 and 3 are coupled ferromagnetically and the moment of atom 1 is antiparallel to them. Let us note that for small value of  $v_1$  the state with all the moments ferromagnetically ordered has almost the same energy. For the Cr trimer the moments of atoms 2 and 3 are antiparallel for small  $v_1$  and the moment of atom 1 is perpendicular to them. Moreover, in the limit  $v_1 \rightarrow 0$  there is no energy dependence on the direction of the moment on atom 1. So, the ordering in the supported dimer is collinear FM for Fe and collinear AF for Cr. The collinear structure of the Fe trimer remains until  $v_1$  reaches a critical value which depends on the strength of the interaction between atoms 2 and 3: this critical value increases from 0.6 to 1.0 when  $v_2$  goes from 0.9 to 1.3 (fig. 1). For  $v_1$  greater than the critical points the moments on the Fe atoms 2 and 3 rotate relatively to the quantisation axis. For equilateral triangle  $\theta_0 = 2\pi/3$  and then approaches  $\pi/2$ . The dependence  $\theta_0 = \theta_0(v_1)$  for the Cr trimer is just the opposite. It monotonically increases with  $v_1$  from  $\pi/2$  to  $\pi$  but also reaches the value  $2\pi/3$  for  $v_1 = v_2$ .

The different behaviour of Fe and Cr trimers is not surprising and reflects the magnetic and structural properties of the bulk materials. Let us note that the electronic, magnetic, and many of the intrinsic properties of the bulk Fe, Cr as well as Fe/Cr interface are described in the Periodic Anderson Model (PAM) [7,8] which is very similar to the model used here.

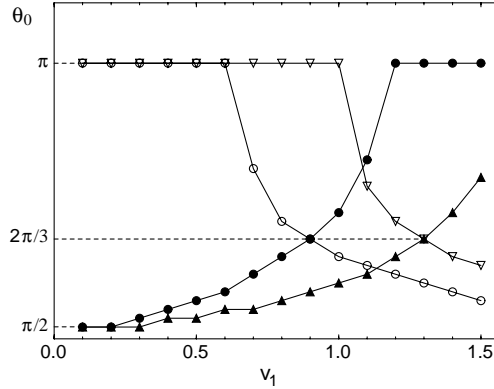


Fig. 1

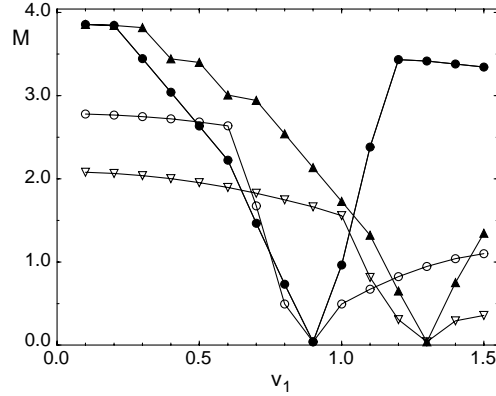


Fig. 2

Fig. 1. – Dependence of the ground state angle  $\theta_0$  between magnetic moments localised on atoms 1 and 2 of the trimer *vs.* hopping integral  $v_1$ . Solid and empty symbols correspond to the Cr and Fe trimers, respectively. Circles and triangles show dependences obtained for  $v_2 = 0.9$  and for  $v_2 = 1.3$ , respectively.

Fig. 2. – The modulus  $M$  of the total magnetic moment of Cr (solid symbols) and Fe (empty symbols) trimers as a function of the hopping integral  $v_1$ . Circles and triangles show dependences obtained for  $v_2 = 0.9$  and for  $v_2 = 1.3$ , respectively.

Fe is found naturally in bcc ( $\alpha$ -phase) and fcc ( $\gamma$ -phase) states.  $\alpha$ -Fe is the typical ferromagnetic material for which each atom has 8 nearest neighbours (nn) and moreover for these 8 nn atoms there are no nn among them. It means that each couple of nn atoms can be considered as dimer. Other atoms do not essentially perturb their states because hopping integrals decrease rapidly with interatomic distance and there are no atoms which are nn for either atom of the dimer under consideration. As already noted, for Fe dimers ( $v_1 = 0$ ) we found FM ordering of the magnetic moments to be preferable.

$\gamma$ -Fe which can be grown as a few-monolayer film on the Cu substrate [9] has AF or even more complicated magnetic structure [10]. Atoms in fcc lattice have 12 nn and each of them has 4 nn among these 12 atoms. This leads to the existence of the magnetic frustrations, which appear already for the simple trimer, and correspondingly to the complex non-collinear behaviour.

Cr like  $\alpha$ -Fe has bcc lattice but for Cr dimers we obtain AF collinear ground state. It is such AF structure that is observed in Cr systems with size less than the spin-density wavelength of bulk Cr.

The modulus of the moments on each atom of the trimer is enhanced relatively to the bulk value for both Fe and Cr cluster. It is connected with the lower number of nn and with the decrease of the width of the  $d$ -band because of it. The increase of the hopping integrals  $v_1$  and  $v_2$  leads to the diminution of the individual moments. For  $v_1 < v_2$ , atom 1 with two bonds  $v_1$  has larger moment than atoms 2 and 3 having one bond  $v_1$  and one  $v_2$ . For  $v_2 < v_1$  opposite ratio between the moments is found.

The modulus ( $M$ ) of the total moment of Cr and Fe trimers as a function of the hopping parameter  $v_1$  is shown in fig. 2.  $M$  is parallel to the quantisation axis. For the Fe trimer the total moment stays almost unchanged for small  $v_1$  for which collinear ordering of the moments takes place. The total moment is antiparallel to the moment of the atom 1. When  $v_1$  is large enough for transition to the non-collinear state (see fig. 1),  $M$  drastically decreases to zero

for  $v_1 = v_2$ . For  $v_1 > v_2$  the total moment takes opposite direction and its modulus increases with  $v_1$ .

For the Cr trimer, small  $v_1$  corresponds to the non-collinear structure with the moment of the atom 1 perpendicular to the moments of atoms 2 and 3. When the moments on atoms 2 and 3 are antiparallel,  $M$  is equal to the moment  $M_1$  of atom 1. With increasing of  $v_1$ ,  $M$  decreases mainly due to the rotation of the moments of atoms 2 and 3. For the equilateral triangle the total moment vanishes and then turns to the opposite direction. After, fast increase of  $M$  takes place till the transition to the collinear state for  $v_2 = 0.9$  (see figs. 1 and 2) where the moment  $M_1$  became antiparallel to  $M_2$  and  $M_3$ . Further increase of the  $v_1$  leads to the slow decrease of  $M$  because of the reduction of the individual moments with increase of the interatomic interaction.

The behaviour of the trimer's magnetic ordering in the limit  $v_2 \rightarrow 0$  is of special interest because this case has to reflect the magnetic ordering in the bulk Fe and Cr. Our calculations show that for small  $v_2$  both Cr and Fe trimers will prefer collinear ordering. For Fe all the moments are ordered ferromagnetically. For the Cr trimer the moment of the atom 1 is antiparallel to the moments of atoms 2 and 3. The value of the moment on the atom 1 for both Fe and Cr is essentially smaller than on the atoms 2 and 3. It is the effect of the reduction of the nearest neighbour's number, because atom 1 has two nearest-neighbour atoms, whereas atoms 2 and 3 have only one. Similar behaviour was obtained by Oda *et al.* [2] for  $\text{Fe}_3$  linear chain and by Cheng and Wang [4] for small Cr clusters.

Self-consistent calculations within the Anderson model give not only the magnetic moments on each atom of the trimer but also the number of  $d$ -electrons which is not constant due to  $s$ - $d$  hybridisation. For Fe and for Cr trimers there is a general tendency of increasing of the average  $d$ -electron number per atom  $N$  vs. the hopping integrals  $v_1$  and  $v_2$ . Such behaviour has much in common with results obtained for rough Fe/Cr interfaces [8]. For rough Fe/Cr interfaces, within collinear PAM, there is a continuous distribution of the Fe and Cr magnetic moments. Calculations give strong correlation between the increase of the magnetic moment and the decrease of the  $d$ -electron numbers on Fe and Cr sites. Manifestation of such behaviour was found in Mössbauer experiments, where linear correlation between the values of hyperfine fields and the chemical shifts measured on the  $^{57}\text{Fe}$  atoms [11] was detected. In the case of trimers the increase of the hopping integrals induces diminution of the individual moments and correspondingly an increase of  $N$  except in the region near the transition from collinear to non-collinear state.

Dependence of the  $d$ -electron number on the parameters of the model has to be taken into account if we compare the energy of the different states. Comparison of the energies can be connected with attraction or repulsion of the atoms in the trimer. However, for this purpose it would be necessary to calculate the energy of  $s$ -electrons in the substrate which were disturbed by the magnetic trimer. We will not discuss this question here, but note that for the Fe trimer the changing of the  $d$ -electron number with  $v_1$  and  $v_2$  is essentially larger than for Cr.

In summary, we show that the non-collinear magnetic structure of supported Cr and Fe trimers depends strongly on the hopping integrals determined by the distance between atoms. If for the free standing clusters this distance can be calculated from the conditions of minimal energy of the state, in the case of supported trimers we have to take into account substrate properties and in particular, the effects of surface reconstruction to find the most probable distances. Reconstruction of the surface which can change the lattice parameters and even the symmetry near the surface can lead to large modification of the magnetic properties of these supported clusters. For trimer clusters this is particularly important for the case with all hopping parameters close to each other. This can be realised, for example, for the fcc metal substrates with (111) surface, when the adsorbed atoms are located on a triangular

lattice. Such non-collinear structure on triangular lattice shows very complex multicritical temperature dependence [12].

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This work was supported by INTAS project No. 960531. VU acknowledges the Alexander von Humboldt foundation for European fellowship at IPCMS (Strasbourg) and Prof. E. KISKER for his hospitality during a research stay at Heinrich Heine Universität, Düsseldorf.

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