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1994 J. Phys.: Condens. Matter 6 L259

(http://iopscience.iop.org/0953-8984/6/18/001)

J. Phys.: Condens. Matter 6 (1994) L259–L264. Printed in the UK

LETTER TO THE EDITOR

The giant magnetic moment and electronic correlation effect in ferromagnetic nitride $Fe_{16}N_2$

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Received 11 January 1994, in final form 1 March 1994

Abstract. The on-site Coulomb interaction correction (LDA+U) and the generalized gradient approximation (GGA) seek to improve upon the accuracy of the local-spin-density approximation (LSDA) in the calculation of the electronic structure of the novel nitride $Fe_{16}N_2$. The non-locality of the exchange–correlation interaction included by the GGA approach does not apparently affect the calculated magnetic moment. However, the LDA+U approach gave a good result which matches the experimentally determined giant magnetic moment more closely than any previous calculations. This fact draws attention to an unusual correlation effect in the nitride $Fe_{16}N_2$ for the first time.

Recently, Komuro *et al* [1] have grown a single-crystal film of $Fe_{16}N_2$ by using a molecular beam epitaxy technique. They reported an unusually high magnetic flux density B_s of 2.8–3.1 T which corresponds to an average moment of 3.1–3.3μ_B per Fe atom. However, the moment of the natural pure Fe metal is only 2.22μ_B per Fe atom. This experiment confirmed the early observation of the giant magnetic moment in this nitride by Kim and Takahashi [2].

Using the standard linear muffin-tin orbital method in the atomic sphere approximation (LMTO-ASA), Sakuma [3] and Min [4] have calculated the electronic and magnetic structure of $Fe_{16}N_2$. Very recently, employing the full potential linearized augmented plane wave (FLAPW) method Coehoorn *et al* [5] have made a similar calculation. They obtained the average moment to be 2.4–2.5μ_B per Fe atom which is about 20% smaller than the experimental measurement. All their calculations are based on the local-spin-density approximation (LSDA). The apparent difference between calculation and experiment might arise from the inappropriate application of the LSDA for this type of magnetic material. In this letter, we consider two corrections to the LSDA: non-locality of exchange–correlation interaction and a strong correlation effect.

In the nitride $Fe_{16}N_2$, there is one type of site for the N atom and three types of non-equivalent crystalline site for the Fe atoms in a distorted body-centred-tetragonal (BCT) structure unit cell. The distances between two Fe atoms in the three types of Fe site are 2.88 Å, 2.81 Å and 2.56 Å respectively, which are much larger than that in natural Fe metal, i.e. 2.42 Å. Undergoing the lattice expansion and distortion, the electronic density should increase inhomogeneity in the unit cell and produce non-spherical distortion over a spherical distribution of electrons in the atoms. The GGA approach with non-locality of exchange–correlation interaction deals with inhomogeneity and non-sphericity of the density [6, 7].

0953-8984/94/180259+06$19.50

Nevertheless, our practice calculation in $Fe_{16}N_2$ does not give an apparent enhancement of the magnetic moment.

Another difference is the stronger correlation effect. From the point of view of the electronic band concept, the large magnetic moment corresponds to an enhancement of both the exchange splitting and the repulsion of electronic occupancy between spin-up and spin-down states. With regard to these two factors, the many-body correlation interaction between electrons plays a key role. A famous example is the Mott metal–insulator transition. In fact, the correlation effect is not adequately included in the LSDA scheme. Now, a convenient method of handling the correlation effect in the calculation is the addition of an on-site Coulomb interaction in the standard local-density-approximation framework, named LDA+U by Anisimov *et al* [8]. In this letter, we apply a stronger correlation effect correction to LDA and adopt the LDA+U formula to study the electronic and magnetic structure of the novel nitride $Fe_{16}N_2$. The calculated magnetic moment obtained by us more closely resemble the experimental results than any previous calculations.

In the following, after a brief description of both GGA and LDA+U approaches, the calculated electronic structure and magnetic moment will be presented.

In the general density functional theory, the exchange–correlation energy of a system of electrons is defined as a functional of up- and down-spin electronic density. It is a non-local functional of electronic density. But in the LSDA, this exchange–correlation energy has been approximately represented as a function of uniform local spin-density neglecting the non-locality. To involve the non-local effect, Langreth *et al* [6] have developed generalized gradient approximations (GGAs) for the exchange–correlation energy

$$E_{xc}^{GGA}[n_\uparrow, n_\downarrow] = \int d^3r f(n_\uparrow n_\downarrow \ \nabla n_\uparrow \ \nabla n_\downarrow) \tag{1}$$

where the electronic density $n(\boldsymbol{r}) = n_\uparrow + n_\downarrow$, n_σ ($\sigma = \uparrow, \downarrow$) is the density of electrons with spin σ, and ∇ is a gradient operator. Recently, Perdew and Wang [7] have presented a unified real-space-cutoff construction of a GGA for exchange and correlation. The details of this formula can be found in [7].

Another approach is LDA+U with a stronger correlation effect. In the LSDA theory, the many-body correlation effect between electrons is inadequately considered in the Kohn–Sham single-electron equations. The LDA+U method used by Anisimov *et al* [8] for Mott insulators has a convenient form for implementation in the Kohn–Sham equation. In this method, the total energy functional of a system is postulated as

$$E = E^{LDA} + \frac{1}{2}\sum_{i,m,m',\sigma} U(n_{im\sigma} - n^0)(n_{im'-\sigma} - n^0) + \frac{1}{2}\sum_{i,m,m',\sigma}^{m\neq m'} (U - J)(n_{im\sigma} - n^0)(n_{im'\sigma} - n^0) \tag{2}$$

where E^{LDA} is the usual spin-independent LDA total energy, $n_{im\sigma}$ is the number operator of the m-orbital electron with spin σ at the ith site and n^0 is the average occupancy of one d orbital ($n^0 = n_d/10$). Finally, the parameters U and J are identified with the LDA Hubbard U and the Stoner parameter I respectively. The corresponding single-electron potential is given by

$$V = V^{LDA} + U\sum_{m'}(n_{m',-\sigma} - n^0) + (U - J)\sum_{m'\neq m}(n_{m',\sigma} - n^0) \tag{3}$$

where V^{LDA} is the LDA potential corresponding to the charge density with the number of d electrons given by $n_d = \sum_{m\sigma} n_{im\sigma}$.

In order to calculate the U and J, the method submitted by Han *et al* [9] is adopted. The parameter U can be evaluated by using the following formula

$$U = \int \frac{\rho_d(r - R_i)A_d^2(r' - R_i)}{|r - r'|} e^{-k|r-r'|}\, dr\, dr' \tag{4}$$

where $\rho_d(r - R_i)$ is the total density of d electrons in the corresponding Fe atom (the number of d electrons is different for Fe(1), Fe(2) and Fe(3) respectively), $A_d(r - R_i)$ is the 3d orbital atomic wavefunction, k is the screening constant and J is selected to be $\sim U/10$. The quantity in formula (4) is equivalent to the U parameter given in [8], i.e. the Coulomb energy cost to place an additional electron at the considered Fe atom.

Table 1. The calculated magnetic moments and occupation number of the electrons in the nitride $Fe_{16}N_2$.

Method	Sites		$n_\uparrow$	$n_\downarrow$	$n_\uparrow + n_\downarrow$	$n_\uparrow - n_\downarrow = m(\mu_B)$
LSDA	Fe(1)	3d	4.43	2.27	6.70	
		Total	5.06	3.06	8.12	2.00
	Fe(2)	3d	4.57	2.01	6.58	
		Total	5.24	2.73	7.97	2.51
	Fe(3)	3d	4.78	1.74	6.52	
		Total	5.39	2.41	7.80	2.98
	N	Total	2.40	2.41	4.81	−0.01
GGA	Fe(1)	3d	4.39	2.20	6.59	
		Total	5.12	3.01	8.13	2.11
	Fe(2)	3d	4.60	1.99	6.59	
		Total	5.27	2.72	7.99	2.55
	Fe(3)	3d	4.77	1.78	6.55	
		Total	5.40	2.48	7.88	2.92
	N	Total	2.50	2.51	5.01	−0.01
LDA+U	Fe(1)	3d	4.50	2.08	6.58	
		Total	5.24	2.88	8.12	2.36
	Fe(2)	3d	4.69	1.88	6.57	
		Total	5.37	2.62	7.99	2.75
	Fe(3)	3d	4.93	1.41	6.34	
		Total	5.63	2.10	7.73	3.53
	N	Total	2.40	2.41	4.81	−0.01

We employed the standard LMTO-ASA band calculation method to study the correlation effect. The U value is calculated from the embedded cluster method by (4). The wavefunction is obtained from self-consistent calculation of three relative cluster models for Fe atoms on different sites in the unit cell and the screening constant k is taken as 0.5. Because the atoms Fe(1), Fe(2) and Fe(3) are in three types of non-equivalent crystalline sites and possess different numbers of electrons, the calculated U parameters are different for these atoms. The obtained U values are 0.08 Ryd for Fe(1), 0.10 Ryd for Fe(2), and 0.29 Ryd for Fe(3) respectively. The meaning of these U parameters for the metallic-like

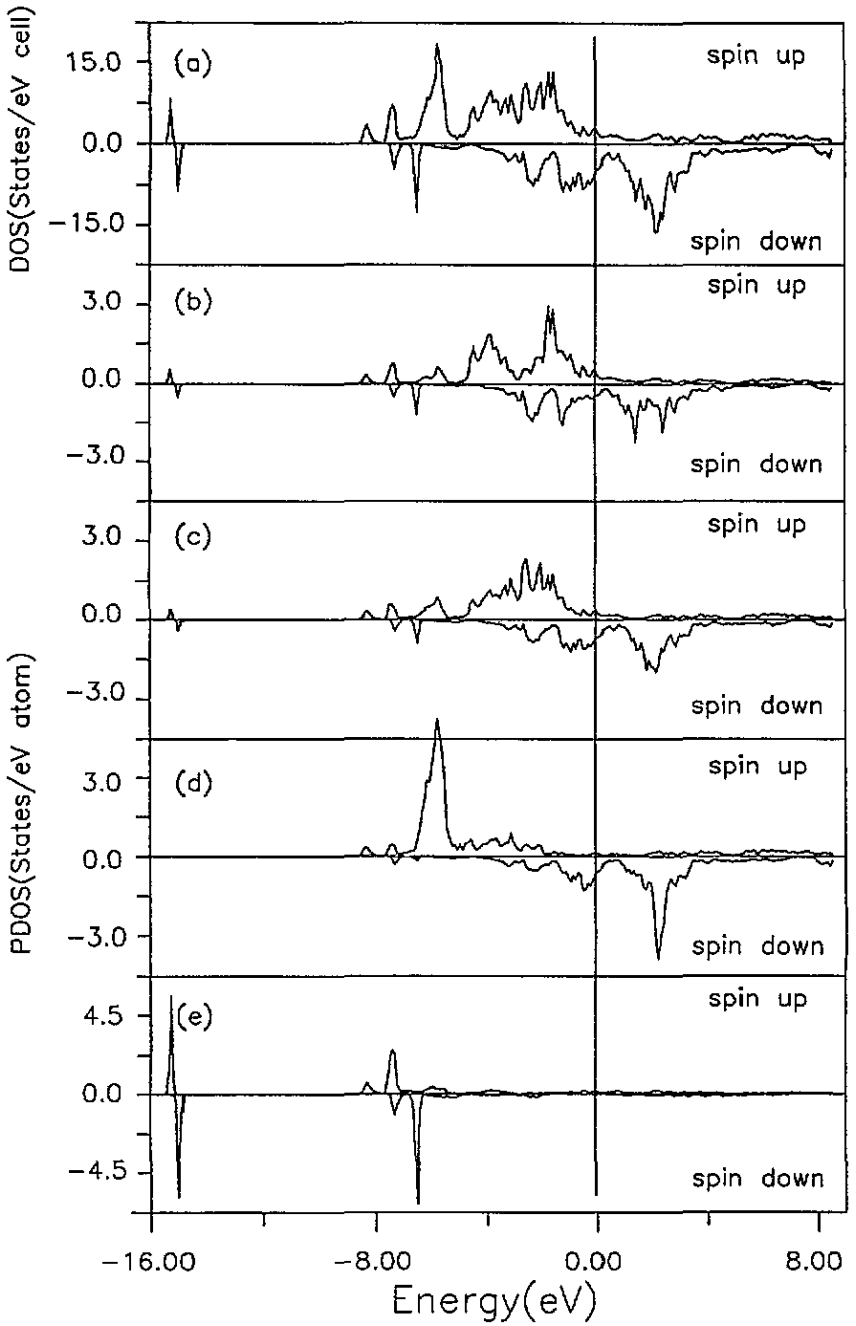

Figure 1. The density of states of nitride $Fe_{16}N_2$ calculated by the LDA+U approach: (*a*) total DOS, (*b*) partial DOS for Fe(1), (*c*) partial DOS for Fe(2), (*d*) partial DOS for Fe(3) and (*e*) partial DOS for N respectively.

compound $Fe_{16}N_2$ will be discussed later. The atomic radius should be selected to satisfy

$$V = \frac{4\pi}{3} \sum_i S_i^3 Q_i.$$

V is the volume of the unit cell, S_i is the atomic radius of ith-type atoms in the unit cell and Q_i is the number of ith-type atoms. The value of $\alpha = S_{Fe}/S_N$ is taken as 1.2 for $Fe_{16}N_2$ in our calculation. The formulation of the LDA+U method depends on the choice of a basis set. The complex types of LMTO--basis set were used here. Other details of the calculation will be published elsewhere.

The calculated magnetic moments and occupation numbers are listed in table 1. The results based on the LSDA in the LMTO-ASA are listed in the first section of this table for comparison. The average magnetic moment of $2.53\mu_B$ per Fe atom calculated based on the GGA is still much smaller than the value measured by Kim and Komuro *et al* [1,2]. There is no significant difference in magnetic moments between GGA and LSDA. On the other hand, the LDA+U calculation results in an average magnetic moment of $2.85\mu_B$ per Fe atom, which more closely matches the experimental measurement than any previous calculations. The electronic densities $n_\uparrow + n_\downarrow$ of the three non-equivalent Fe sites are almost invariant for the three calculation approaches. This means that the charge transfer between 4s, 4p and 3d orbitals is similar and small. But, the occupation number in different spin subbands was much more affected due to the inclusion of the on-site Coulomb interaction. For example, the 3d-orbital electronic densities ($n_\uparrow$, $n_\downarrow$) in site Fe(3) are (4.78, 1.74) for LSDA and (4.77, 1.78) for GGA respectively, which are almost identical. However, the densities ($n_\uparrow$, $n_\downarrow$) in site Fe(3) are (4.93, 1.41) for the LDA+U approach, which gives a larger difference of occupation number between spin-up and spin-down subbands than that for both the LSDA and GGA approaches. This is as a result of the on-site Coulomb interaction in the strong correlation effect which produces a stronger repulsion of electronic occupancy between spin-up and spin-down states.

The total density of states (DOS) and partial DOS of the nitride $Fe_{16}N_2$ in the LDA+U approach with LMTO-ASA method are shown in figure 1. The exchange splitting of electrons between spin-up and spin-down states based on the LDA+U calculation is apparently larger than that for the LSDA calculation. This is another aspect of the correlation effect in the electronic system.

Due to the many-body effect of screening, there is ambiguity in the first-principles parameter calculation. The values for U of 0.44 Ryd and J of 0.07 Ryd were used by Anisimov *et al* [8] in the insulator FeO with small screening effect. But in the metal the screening effect is stronger than in the insulator, so the U value should be small: 0.05 Ryd for Fe and 0.037 Ryd for Ni [9]. In our LDA+U approach, the calculated U parameters of $Fe_{16}N_2$ are 0.08 Ryd for Fe(1), 0.10 Ryd for Fe(2) and 0.29 Ryd for Fe(3) respectively, which are reasonably positioned as median values between the insulator FeO and the metal Fe and Ni. Until now, the methods of calculating U have given approximate values suitable for estimation. The problem of improving the estimation still stands.

In conclusion, the electronic and magnetic structure based on LDA+U draws attention to the unusually strong correlation interaction between electrons inside the novel nitride $Fe_{16}N_2$ for the first time.

This work is supported by the National Laboratory of Magnetism, Chinese Academy of Sciences, Beijing.

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