ELSEVIER

Journal of Magnetism and Magnetic Materials 240 (2002) 334–336

www.elsevier.com/locate/jmmm

On the origin of the giant magnetic moments of Fe and Co in Cs Films

G.Y. Guo^{a,b,*}

^aDepartment of Physics, National Taiwan University, 1 Sec. 4, Roosevelt Road, Taipei 106, Taiwan

^bSynchrotron Radiation Research Center, Hsinchu 300, Taiwan

Abstract

To unravel the mystery of the recently observed giant magnetic moments of Fe and Co in Cs films, orbital-polarization corrected relativistic spin density functional calculations have been performed. Unlike other transition-metal systems where the orbital magnetic moments are quenched, Fe and Co in Cs as well as in other alkali metals are found to possess a giant orbital moment of $2\text{--}3\mu_B$ along with a large spin moment. Also, these free atom-like spin and orbital magnetic moments in Cs would not be squashed under large lattice contractions up to 23% around the impurity atoms. The induced moments on the host atoms are small. The results offer an explanation for the origin of the giant magnetic moments of Fe and Co in Cs films. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: 3d impurities; Alkali metals; Magnetic moments; Orbital moments

It is reported recently [1] that Fe and Co impurities on the surface and in the interior of thin Cs films have a large magnetic moment of about 7 and $8\mu_B$, respectively. Since bulk Fe and Co have a magnetic moment of only 2.2 and $1.7\mu_B$ [2], respectively, the observed moments were justifiably considered to be giant [1]. There is a well known system with giant moments: 3d transition-metal impurities in a palladium host possess a large moment ($9\text{--}12\mu_B$ for Fe and Co in Pd) [3]. For transition-metal compounds, this perhaps had been the only example that have giant moments. The reason is that the Fermi level in bulk Pd is located at the upper edge of the 4d band with a large density of states at it. As a result, Pd is a highly enhanced paramagnet. The presence of a 3d magnetic impurity induces significant spin moments of the order of $0.1\mu_B$ on the neighboring Pd atoms even including those Pd atoms being many atomic shells away [3,4]. Consequently, the total magnetic moment of the 3d impurity plus the surrounding palladium atoms is gigantic, with the majority being

made up of the induced spin moments on the Pd atoms. However, alkali metals are the good examples of nearly free electron systems, as described in many solid state text books [5]. Indeed, the Fermi surface of Na, K and Rb determined by de Haas-van Alphen experiments deviates from that of the free-electron model by 1 percent at worst [5]. Thus, alkali metals are a weak paramagnet at best and the giant moments in Cs films would not be expected to have the same origin as that of the palladium systems. The presence of the giant moments of Fe and Co in Cs films is therefore a mystery.

In order to find the origin of the observed giant moments of Fe and Co in Cs films, I have calculated from first principles, the magnetic moments and other properties of Fe and Co in alkali metals (Li, Na, K, Rb and Cs) and also of Fe in transition-metals Ag and Pd. Some results for Co in Cs and for Fe in K, Rb, Cs, Ag and Pd have been reported in Ref. [6]. These calculations are based on relativistic spin density functional theory [7] with the orbital-polarization corrections (OPC) (see Ref. [8] and references therein). Note that, in the present implementation of the OPC, both the Racah parameter and spin-decomposed orbital angular momentums are recalculated in each self-consistent iteration and thus it

*Corresponding author. Tel.: +886-2-23626937;
fax: +886-2-23639984.

E-mail address: gyguo@phys.ntu.edu.tw (G.Y. Guo).

Table 1

Calculated spin (m_s), orbital (m_o), total ($m_t = m_s + m_o$) magnetic moments and magnetic dipole moment (T_z) of Fe (Co) in Li, Na, K, Rb, and Cs^a

System	m_s (μ_B)	m_o (μ_B)	m_t (μ_B)	$7T_z$ (μ_B)	M_t (μ_B)	a (Å)
Co in Cs	2.67	2.95	5.62	0.23	5.21	6.05
Fe in Cs	3.86	2.27	6.13	−1.48	5.45	6.05
Fe in Rb	3.79	2.32	6.11	−1.38	5.61	5.59
Fe in K	3.68	2.39	6.07	−1.25	5.76	5.23
Fe in Na	3.42	2.34	5.76	−0.92	5.62	4.23
Fe in Li	3.03	1.84	4.88	−0.30	4.69	3.49
BCC Fe	2.25	0.08	2.33	—	—	2.87

^a M_t denotes the total magnetic moment per supercell, and a the BCC lattice constants used in the calculations [5].

is parameter free [8]. The relativistic spin-polarized linear muffin-tin orbital method [9] was used. The Fe and Co impurities in the alkali metals were modelled by a $3 \times 3 \times 3$ BCC supercell with one Fe atom and 53 alkali metal atoms per unit cell. It is expected that the calculated magnetic moments would not be affected if the supercell size were increased. Indeed, the magnetic moments of Fe (Co) in the alkali metals calculated using a $2 \times 2 \times 2$ BCC supercell (16 atoms/cell) are close to that obtained by using a $3 \times 3 \times 3$ BCC supercell. For example, the calculated Fe (Co) spin and orbital moments in the two cases differ by only 2% (see Tables 1 and 2). The results of these calculations predict, as expected, that the induced magnetic moments on the host alkali atoms are small (within $0.02 \mu_B$ /atom) and antiparallel to the Fe (Co) moment. However, it is found that Fe (Co) in Cs possess a giant orbital moment of $2.3 \mu_B$ ($3.0 \mu_B$) as well as a large spin moment of $3.9 \mu_B$ ($2.7 \mu_B$) (Table 1). At first glance, this finding is highly surprising because in transition-metal solids the orbital moment of the d valence electrons is generally quenched due to the crystal field splitting or the hybridization of the d-orbitals with that of neighboring atoms [5]. For example, bulk Fe has an orbital moment of only $0.09 \mu_B$ and bulk Co, $0.14 \mu_B$ [2]. This theoretical finding nonetheless sheds light on the mystery of Fe and Co in Cs films [1]. The calculated total angular moment is $3.9 \mu_B$ for Fe in Cs and $4.1 \mu_B$ for Co in Cs [6], in good agreement with the experimental values (3.5 and $4.0 \mu_B$) [1]. The larger total magnetic moments reported [1] could be attributed to the use of Landé-factor g of 2 which is appropriate if the orbital moments were negligible [5]. On second thoughts, free ion-like magnetic behavior of Fe and Co in Cs, Rb and K were deduced from local magnetic susceptibility and 3d-spin dynamics experiments long ago in the 1980s by Riegel and coworkers [10,11]. Furthermore, analysis of the measured local susceptibilities [12] suggested negligible contributions arising from induced host atom magnetizations, in accordance with the present calculations.

Table 2

Calculated spin (m_s), orbital (m_o) and total (m_t) magnetic moments of Fe in bulk Cs as a function of Fe–Cs bondlength^a

Bondlength	98%	91%	87%	82%	77%
m_s	3.83	3.74	3.68	3.58	3.44
m_o	2.30	2.31	2.32	2.34	2.30
m_t	6.13	6.05	6.00	5.92	5.74
M_t	5.77	5.74	5.74	5.64	5.37

^a M_t denotes the total moment per supercell. All the moments are in units of μ_B . The Fe–Cs bondlength is referred to the ideal value of 5.24 Å .

However, no theoretical calculation nor direct measurement of the orbital magnetic moments in these alkali metal systems has been reported before. Thus, it would be highly desirable to perform an X-ray Fe(Co) $L_{2,3}$ -edge magnetic circular dichroism (XMCD) measurement which can probe spin and orbital moments element-specifically [2], for Fe (Co) in alkali metals. In this context, it is interesting to note that the calculated magnetic dipole moment (T_z) [13] on the Fe impurity in Cs, Rb, K and Na is also huge (Table 1), and hence they cannot be neglected when deriving the spin magnetic moment from the XMCD measurements via the spin sum rule [2,13].

The orbital moments in a transition-metal system result from the spin–orbit splitting of the valence d states. It is stated in solid state text books [5] that in 3d transition-metal compounds, the weak spin–orbit coupling of the valence d electrons is suppressed by the crystal fields because of the strong interaction of the d orbitals with neighboring atoms. Thus, the orbital moment of the valence electrons in these systems is quenched [5]. A good measure of the crystal field strength is the energy separation of the d– t_{2g} and d– e_g states in the cubic metals. My calculations show that for bulk Fe, this separation is about 1.6 eV , being much larger than the spin–orbit splitting of 0.04 eV . In

contrast, this separation for Fe in Cs is much weaker, being around 0.01 eV for spin-down band and 0.002 eV for spin-up band. This finding is consistent with negligible crystal field splitting (within 0.025 eV) of Fe in Cs deduced from local magnetic susceptibility and 3d-spin dynamics experiments [10]. Clearly, the very small crystal field splittings and hence the large orbital magnetic moments of Fe and Co in Cs result from very weak interaction between the impurity atoms and the host Cs atoms. This weak impurity–host interaction are due to two factors. Firstly, Fe (Co) spin-up d band, spin-up and down s bands of Fe (Co) in Cs are located below the Cs conduction band and thus do not hybridize with Cs sp orbitals [6]. Though in overlap with the Cs sp bands, Fe (Co) spin-down d band forms a narrow resonant peak with a width of about 0.05 eV, due to weak interaction with Cs sp bands.

Secondly, the impurity–host atom distance in Fe (Co) in Cs is large, being about twice that of, e.g., nearest-neighbor Fe–Fe distance in BCC iron (Table 1). With such large impurity–host separations, substantial local structural relaxations could be expected. Indeed, large lattice contractions (up to 20%) around the 3d impurities in alkali metals K, Rb and Cs have been proposed [12]. To see whether the atomic orbital moments of the Fe and Co impurities in Cs would collapse or not under large impurity–host bondlength contractions, I present in Table 2 the calculated spin and orbital magnetic moments of Fe in Cs as a function of nearest-neighbor Fe–Cs bondlength. A $2 \times 2 \times 2$ BCC supercell with one Fe atom and 15 Cs atoms per unit cell was used. Calculations for five Fe–Cs bondlengths obtained by using five Cs atomic sphere radii with the Fe atomic sphere radius fixed to that of BCC Fe, were performed. Clearly, a reduction of Fe–Cs bondlengths by at least 23% would not significantly change the magnetic moments of Fe in Cs as well as the total

magnetic moment per supercell (Table 2). This is consistent with the finding that the calculated spin and orbital magnetic moments in Fe in Rb, K and Na are only slightly smaller than those in Fe in Cs (Table 1). Note that the lattice constant of BCC Na is 30% smaller than that of BCC Cs. Even Fe in Li whose lattice constant is over 40% smaller than that of BCC Cs, have large spin and orbital magnetic moments (Table 1). It is gratifying that large magnetic moments ($5\text{--}6 \mu_B$) of Fe and Co have also been observed very recently in Na films with Fe and Co impurities [14].

The author thanks National Science Council of the Republic of China for financial supports (NSC 89-2112-M002-025, NSC 90-2112-M002-008).

References

- [1] H. Beckmann, G. Bergmann, *Phys. Rev. Lett.* 83 (1999) 2417.
- [2] C.T. Chen, et al., *Phys. Rev. Lett.* 75 (1995) 152.
- [3] G.J. Nienwenhuys, *Adv. Phys.* 24 (1975) 515.
- [4] R. Zeller, *Model. Simul. Mater. Sci. Eng.* 1 (1993) 553.
- [5] N.W. Ashcroft and N.D. Mermin, *Solid State Physics*, Saunders College, Philadelphia, 1976.
- [6] G.Y. Guo, *Phys. Rev.* 62 (2000) 14609.
- [7] A.H. MacDonald, S.H. Vosko, *J. Phys. C* 17 (1979) 3355.
- [8] G.Y. Guo, *Phys. Rev. B* 55 (1997) 11619.
- [9] H. Ebert, *Phys. Rev.* 38 (1988) 9391.
- [10] D. Riegel, et al., *Phys. Rev. Lett.* 57 (1986) 388.
- [11] K.D. Gross, D. Riegel, *Phys. Rev. Lett.* 61 (1988) 1249.
- [12] K.D. Gross, D. Riegel, R. Zeller, *Phys. Rev. Lett.* 63 (1989) 1176.
- [13] P. Carra, et al., *Phys. Rev. Lett.* 70 (1993) 694.
- [14] G. Bergmann, M. Hossain, *Phys. Rev. Lett.* 86 (2001) 2138.