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Giant orbital moments of Fe and Co in alkali metals Cs, Rb, and K

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Orbital-polarization corrected relativistic spin-density-functional calculations of Fe and Co in alkali metals (K, Rb, and Cs) predict that unlike other transition-metal systems where the orbital magnetic moments are quenched, Fe and Co in alkali metals possess a giant orbital moment of 2–3 μ_B along with a large spin moment. The induced moments on the host atoms are small. The large orbital moments result from the weak interaction between the 3d impurities and the host atoms. The results reveal the origin of the giant moments observed in Fe and Co in Cs films.

Recently, it was reported[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 8μ_B, respectively. This interesting result was found in anomolous Hall effect experiments. Since bulk Fe and Co have a magnetic moment of only 2.2 and 1.7μ_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 (9–12μ_B for Fe and Co in Pd).[3,4] 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 on 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 0.1μ_B on the neighboring Pd atoms even including those Pd atoms being many atomic shells away.[3–5] Consequently, the total magnetic moment of the 3d impurity plus the surrounding Pd atoms is gigantic, with the majority being made up of the induced spin moments on the Pd atoms. However, alkali metals are a good example of nearly-free-electron systems, as described in many solid-state text books.[6] 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% at worst.[6] 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, we have calculated from first-principles the magnetic moments and other properties of Fe and Co in some alkali metals (K, Rb, and Cs) and also of Fe in transition metals Ag and Pd. The results of these calculations predict as expected that the induced magnetic moments on the host alkali atoms are small (within 0.02μ_B/atom). However, we find that Fe (Co) in the alkali metals possesses a giant orbital moment of 2.3μ_B (3.0μ_B) as well as a large spin moment of 3.9μ_B (2.7μ_B). This finding is surprising at first glance because in transition-metal solids the orbital moment of the d valence electrons is generally quenched due to the crystal-field spitting or the hybridization of the d orbitals with that of neighboring atoms.[6] For example, bulk Fe has an orbital moment of only 0.09μ_B and bulk Co, 0.14μ_B.[2] Even in ultrathin Co/Au multilayers in which the orbital magnetization is enhanced, the orbital moments of Co atoms are a small fraction (about 0.2μ_B) of 3.0μ_B.[7] The results of the present calculations are thus interesting and important. First of all, this theoretical finding sheds light on the mystery of Fe and Co in Cs films[1] mentioned above. The calculated total angular moment is 3.9 for Fe in Cs and 4.1 for Co in Cs, in good agreement with the experimental values (3.5 and 4.0).[1] The larger total magnetic moments reported in Ref. 1 could be attributed to the use of Lande factor g of 2 which is appropriate if the orbital moments were negligible.[6] Second, if the prediction confirmed by experiments, e.g., x-ray magnetic circular dichroism,[2] Fe and Co in alkali metals would be a rare transition-metal system with giant orbital moments and could provide a valuable system for exploring orbital magnetism and for technological applications. Orbital magnetization is known to be closely related to such interesting phenomena as magneto-optical effect,[8] magnetostriction and magnetocrystalline anisotropy.[7,9]

The magnetic moments in Fe (Co) in bcc Cs were determined by performing all-electron self-consistent spin-polarized electronic band-structure calculations. For comparison, the same calculations have also been carried out for Fe in bcc K (Rb) and in fcc Ag (Pd). The well established linear muffin-tin orbital (LMTO) method[10] has been used. These calculations are based on the first-principles density-functional theory with the local spin-density approximation (LDA).[11] The accurate local exchange-correlation potential parametrized by Vosko *et al.*[13] was used. The basis functions for all the atoms used were s, p, and d MTO's. The Fe (Co) atoms in the alkali metals were assumed to be substitutional impurities and were modeled by a $3\times3\times3$ bcc supercell with one Fe (Co) atom and 53 Cs (K, Rb) atoms per unit cell. The Fe impurities in Ag (Pd) were modeled by a $2\times2\times2$ fcc supercell with one Fe atom and 31 Ag(Pd) atoms per unit cell. As will be shown below, the induced moments on the near-neighbor (NN) host atoms in all the systems except Fe in Pd are small, and hence 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 $2\times2\times2$ supercell (16 atoms/cell) are close to that obtained by using a $3\times3\times3$ supercell. For example, the calculated Fe (Co) spin and orbital moments in the two cases differ by only 2%. The atomic-sphere radii used were determined from the measured unit-cell volumes of pure Fe, Co, K, Rb, Cs, Ag, and Pd metals.[6] Thus, the lattice constants of the supercells for Fe (Co) in Cs (K, Rb) are about three times that of bulk Cs (K, Rb), respectively, and those for Fe in Ag (Pd) are about twice that of bulk Ag (Pd). Note that there could be structural relaxations around the Fe (Co) atoms in Cs since the NN Fe(Co)-Cs distance in the assumed structure is considerably larger than that of the usual Fe(Co)–transition-metal atoms, e.g., in Fe in Ag. While this possible reduction of the NN Fe-Cs distance must await further experiments (e.g., extended x-ray absorption fine structure), test calculations for Fe in Cs with a reduced lattice constant indicated that a reduction of the Fe(Co)-Cs distance by up to 22% would not change significantly the calculated spin and orbital moments of Fe (Co) in Cs presented below. The number of *k* points in the irreducible Brillouin zone (BZ) wedge used in the tetrahedron BZ integration[14] is 35 for all the systems. Test calculations showed that with these choices of the number of *k* points, the calculated moments converge to within 5%. For the density of states calculations, 455 *k* points is used for all the systems.

The orbital moments in a transition-metal system result from the spin-orbit splitting of the valence *d* states. Thus, to calculate the orbital moments one has to either include the spin-orbit coupling as a perturbation in the Kohn-Sham equation[10] or solve the Kohn-Sham-Dirac equation based on relativistic spin-density-functional theory[15] (RLDA). We choose the latter and use a fully relativistic extension of the LMTO method.[12] It is well known that although (R)LDA calculations describe well the spin moments in many solids, they often give too small orbital moments. For example, for bulk Fe and Co, the theoretical values account for only about 50% of the measured ones.[2] A solution to this defect is to include in the Kohn-Sham equation an orbital-polarization correction[16] (OPC) of $-BL_z^\sigma$ where B is the Racah parameter (for *d* states) and L_z^σ the total orbital momentum for spin σ. Since both B and L_z^σ can be recalculated in every self-consistent iteration, this scheme is parameter free. The OPC has been found to bring the calculated orbital moments in many metallic solids in good agreement with experiments.[16–18] In this paper, we have therefore carried out the RLDA calculations with the OPC included through a recent implementation for the Kohn-Sham-Dirac equation.[18] Because of the time-reversal symmetry breaking and hence the tripling of the irreducible BZ wedge, the number of *k* points used in the RLDA calculations are three times that used in the LDA calculations.

The calculated magnetic moments for Fe in K, Rb, and Cs are summarized in Table I, and that for Co in Cs and Fe in Ag and Pd in Table II. The results of the LDA, RLDA, and RLDA plus OPC calculations are all listed for comparison. Tables I and II show that including OPC typically increases the calculated orbital moments by 30–90 %. Since this increase in the orbital moments due to OPC is important to diminish the discrepancy between the LDA calculations and the experiments,[2,17,18] we will discuss below only the orbital moments obtained by the OPC calculations. The induced orbital moments on the alkali and Ag atoms are all less than $0.01\mu_B$ and are thus not listed in Tables I and II. Table I shows that the calculated spin moment of an iron (cobalt) atom in bulk Cs is 3.9 $(2.7)\mu_B$, being short of 4 $(3)\mu_B$ predicted by Hund's first rule for a free d^6 (d^7) ion.[6] This spin moment reduces slightly as Cs is replaced by lighter alkali metals (Rb, K). It is stated in many solid-state textbooks (e.g., Ref. 6) 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, Hund's second rule proposed for free ions is no longer applicable and the orbital moment of the valence electrons in these systems is quenched.[6] A good measure of the crystal-field strength is the energy separation of the $d-t_{2g}$ and $d-e_g$ of the cubic metals at the BZ center. Our 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. It is thus surprising at first glance that the theoretical orbital moment of an iron or colbalt atom in Cs is gigantic (2.3 or $3.0\mu_B$) (Tables I and II), being 20 times larger that of bulk Fe or Co. As expected, the induced magnetic moments on the host alkali metal atoms in the NN shell are small (about $-0.02\mu_B$). Furthermore, these small induced moments are antiparallel to that of the iron atoms. The induced magnetic moments on the alkali metal atoms in the third NN shell and beyond are negligible. The total magnetic moment of the Fe (Co) in Cs system thus consists mostly of the magnetic moment on the Fe (Co) atom.

TABLE I. Calculated spin (m_s), orbital (m_o) and total ($m_t = m_s + m_o$) magnetic moments as well as magnetic dipole moment (T_z) of Fe in bulk K, Rb, and Cs. The results of local spin-density approximation (LDA), relativistic LDA (RLDA), and RLDA plus the orbital polarization correction (OPC) calculations are all listed for comparison. n_d (n_t) denotes the number of *d* (valence) electrons of Fe. M_t (M_o) denotes the total (orbital) moment per supercell and the superscript *n* denotes the Cs atoms on the *n*th neighbor atomic shell.

System	Atom		LDA (μ_B)	RLDA (μ_B)	OPC (μ_B)
Fe in K	Fe	m_s	3.75	3.75	3.68
		m_o (n_d)		1.26 (6.39)	2.39 (6.45)
		m_t (n_t)	3.75	5.01 (7.43)	6.07 (7.46)
		$7T_z$			-1.25
		M_t (M_o)	3.52	4.65 (1.24)	5.76 (2.35)
Fe in Rb	Fe	m_s	3.86	3.86	3.79
		m_o (n_d)		1.35 (6.30)	2.32 (6.37)
		m_t (n_t)	3.86	5.21 (7.48)	6.11 (7.50)
		$7T_z$			-1.38
		M_t (M_o)	3.46	4.69 (1.33)	5.61 (2.30)
Fe in Cs	Fe	m_s	3.86	3.86	3.86
		m_o (n_d)		1.35 (6.24)	2.27 (6.31)
		m_t	3.86	5.21 (7.53)	6.13 (7.55)
		$7T_z$			-1.48
	$Cs^{1,2}$	m_s	-0.02	-0.02	-0.02
	$Cs^{3,4}$	m_s	-0.01	-0.01	-0.01
		M_t (M_o)	3.46	4.69 (1.36)	5.45 (2.25)

The spin moments in an Fe impurity in Ag are similar to that of Fe in alkali metals, viz., the Fe impurity has a spin moment much larger than that of bulk Fe and the induced

TABLE II. Calculated spin (m_s), orbital (m_o) and total (m_t) magnetic moments as well as magnetic dipole moment (T_z) in Co in bulk Cs and Fe in bulk Ag and Pd. The results of local spin-density approximation (LDA), relativistic LDA (RLDA), and RLDA plus the orbital polarization correction (OPC) are all listed for comparison. n_d (n_t) denotes the number of d (valence) electrons of Fe. M_t (M_o) denotes the total (orbital) moment per supercell and the superscript n denotes the host atoms on the nth neighbor atomic shell.

System	Atom		LDA (μ_B)	RLDA (μ_B)	OPC (μ_B)
Co in Cs	Co	m_s	2.67	2.66	2.67
		m_o (n_d)		2.24 (7.43)	2.95 (7.45)
		m_t (n_t)	2.67	4.90 (8.61)	5.62 (8.64)
		$7T_z$			0.23
		M_t (M_o)	2.11	4.38 (2.23)	5.21 (2.94)
Fe in Ag	Fe	m_s	3.08	3.08	3.07
		m_o (n_d)		0.22 (6.52)	0.68 (6.52)
		m_t (n_t)	3.08	3.30 (7.51)	3.75 (7.51)
		$7T_z$			-0.13
	Ag^1	m_s	-0.01	-0.01	-0.01
		M_t	2.98	3.07	3.52
Fe in Pd	Fe	m_s	3.36	3.35	3.34
		m_o (n_d)		0.07 (6.41)	0.22 (6.41)
		m_t (n_t)	3.36	3.42 (7.62)	3.56 (7.62)
		$7T_z$			-0.003
	Pd^1	m_s	0.28	0.26	0.28
		m_o		0.027	0.028

spin moments on the neighboring Ag atoms are negligibly small (see Tables I and II). On the other hand, the orbital moment ($0.68\mu_B$) of Fe impurity in bulk Ag is small compared with that of the alkali metal systems though it is enhanced relative to that of bulk Fe. This results from a stronger interaction between the Fe d orbitals and the host Ag bands. To see this clearly, we display the LDA density of states (DOS) spectra of the Fe impurities in Cs, Ag, and Pd in Fig. 1. Figure 1 shows that spin-up d band, spin-up and down s bands of Fe in Cs are located below the Cs conduction band and thus do not hybridize with Cs sp orbitals. As a result, they are highly localized and their DOS are a sharp peak located, respectively, at 3.2, 2.7, and 2.0 eV below the Fermi level (E_f) [see Fig. 1(a)]. Though in overlap with the Cs sp bands, Fe spin-down d band forms a narrow resonant peak with an estimated width at half-height of 0.05 eV, due to weak interaction with Cs sp bands. Note that the small Fe DOS component present in the Cs band region [Fig. 1(a)] is due to Fe s orbital. In constrast, spin-up and down d bands of Fe in Ag are much broader [Fig. 1(b)]. Further, a small component of the Fe d DOS extends to the entire Ag d band region. This stronger interaction between the Fe and Ag d electrons is also seen in the size of the Fe $3d$ crystal-field spitting in Fe in Ag which is about 0.10 eV (spin-down band) compared with 0.01 eV (spin-down band) for Fe in Cs. The spin moment of the Fe impurity in Pd is in the same order of magnitude as that of Fe in Ag and alkali metals (see Tables I and II). However, because of the very strong interaction between the d electrons of Fe and Pd atoms as revealed in the almost complete mixing of the Fe and Pd spin-up DOS in the entire valence band [see Fig. 1(c)], the induced moments on the near-neighbor host Pd atoms are considerable (Table II) and extended to several next-neighboring atomic shells.[5] On the other hand, the very strong interaction between the d electrons of Fe and Pd atoms in the Pd system quenches the orbital moment of the Fe atoms ($0.2\mu_B$). The Fe $3d$ crystal-field splitting defined above in this system is about 0.27 eV, being much larger that in Fe in Cs and also larger than the spin-orbit splitting (0.04 eV).

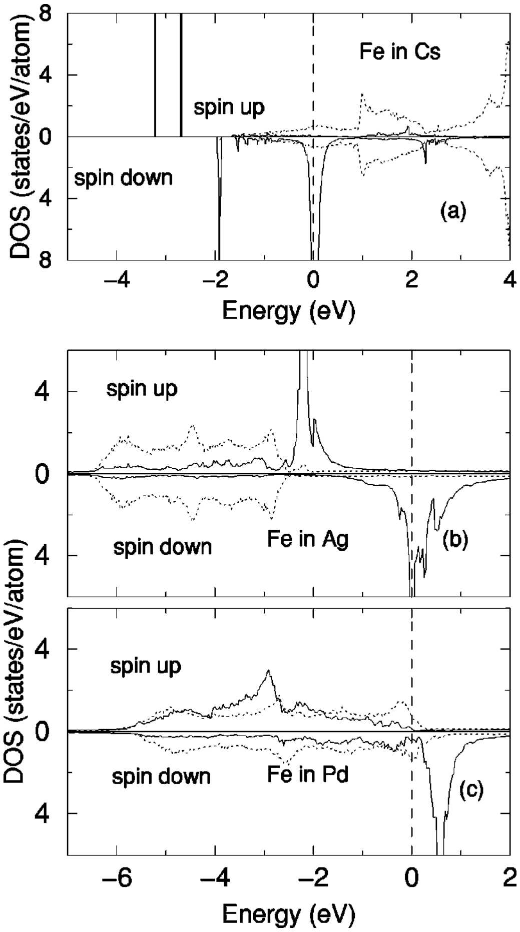

FIG. 1. Density of states (DOS) of Fe in Cs (a), Ag (b), and Pd (c). Solid curves are for the Fe atom. Dotted curves in (a), (b), and (c) denote the averaged DOS for the Cs, Ag, and Pd atoms, respectively. The Fermi level is at the zero energy.

The reported total magnetic moment is $7\mu_B$ for Fe in Cs and $8\mu_B$ for Co in Cs.[1] The experimental values appear to be larger than the corresponding theoretical values of 5.5 and $5.2\mu_B$. However, this direct comparison should be made with caution. In Ref. 1, the total angular momentum ($J=L+S$) of the systems was derived by fitting a Brillouin function[6] to the measured anomalous Hall resistances (AHR) with assumptions that the AHR is proportional to the magnetization and that the Lande factor $g(JLS)=2$. The total angular momentum (J) was found to be 3.5 for Fe in Cs and 4.0 for Co in Cs, in reasonable agreement with the corresponding theoretical values of 3.9 and 4.1. The total magnetic moments were obtained by using expression $M_t = gJ\mu_B$.[1] The assumption that $g=2$ is correct if the orbital angular momentum $L=0$. The assumption was obviously reasonable since no transition-metal system had been known to possess a significant orbital moment before. For Fe and Co in alkali metals, however, the present calculations show that the orbital moments are huge. As a result, the g estimated using the calculated orbital and spin moments is significantly reduced. This g value is about 1.42 (1.28) for Fe (Co) in Cs, being close to $\frac{3}{2}$ $(\frac{4}{3})$ for a free Fe^{2+} (Co^{2+}) ion.[6] If these g factors were used, the total magnetic moments would have been 5.0 for Fe in Cs and $5.1\mu_B$ for Co in Cs, being close to the theoretical results. This would suggest that another analysis of the AHR data[1] might be needed. On the other hand, other magnetic experiments will be useful. In particular, x-ray magnetic circular dichroism (XMCD) has recently emerged as an element-specific probe of spin and orbital magnetic moments in solids.[19,20,2] The prediction of the giant orbital moments of Fe and Co in alkali metals could be checked by a soft x-ray Fe(Co) $L_{2,3}$-edge MCD measurement. Furthermore, the negligibly small induced moments on the host alkali atoms could be verified by measuring e.g., K K-edge MCD spectrum. It should be pointed out that unlike other transition-metal intermetallics where the magnetic dipole moments are small,[20,21] the magnetic dipole moment (T_z) (Ref. 22) on the Fe impurity in alkali metals is large (see Table I) and cannot be neglected when deriving the spin moment from the XMCD measurements via the spin sum rule.[20,2]

Summarizing, in order to reveal the origin of the recently observed giant moments of Fe and Co in Cs films, we have carried orbital-polarization-corrected relativistic spin-density function calculations for Fe and Co in some alkali metals (K, Rb, and Cs). These calculations predict that Fe and Co in the alkali metals possess a giant orbital magnetic moment. Since RLDA-OPC calculations have been found to give accurate orbital moments, Fe and Co in the alkali metals are expected to be the first transition-metal systems with giant orbital moments. The predicted giant orbital moments together with the large spin moments on the Fe and Co impurities are believed to be the origin of the giant moments observed in Fe and Co in Cs films. It is hoped that this interesting finding would prompt further experimental investigations into these systems, in particular, direct magnetization measurements such as x-ray magnetic circular dichroism.

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[22] $T_z = \langle \beta \hat{T}_z \rangle$ with $\hat{T}_z = \frac{1}{2}[\sigma - 3\hat{r}(\hat{r}\cdot\sigma)]_z$ where β and σ are the Dirac and Pauli matrices, respectively.