Recent progress in fabrication and characterization of the magnetic nano-particles and thin films based on the ordered $L_1_0$ CoPt and FePt alloys renewed interest in understanding the mechanisms contributing to the large magneto-crystalline anisotropy of these materials. While the earlier studies were primarily motivated by permanent magnet applications, current research efforts are focused on the use of CoPt and FePt alloys for the high density magnetic recording. The large and controllable magnetic anisotropy energy (MAE) is then a crucial property to overcome a superparamagnetic limit.

The chemically ordered $L_1_0$ phase of FePt has large uniaxial MAE ($\approx 6.6 \times 10^5 \text{erg/cc}$) which is almost by two orders of magnitude higher than their disordered fcc phase (a dramatic MAE increase with chemical ordering is also typical for other alloys of this kind: CoPt and FePd). The cubic symmetry is broken in $L_1_0$ phase by (i) stacking of alternate planes of 3$d$ element (Fe or Co) and Pt along [001] direction; (ii) by tetragonal distortion due to 3$d$ and 5$d$ atomic size mismatch. For the tetragonal crystal with uniaxial symmetry, the MAE depends on partial polarization angle $\theta$ as,

$$E = K_1 \sin^2 \theta + K_2 \sin^4 \theta + ...$$  \hspace{1cm} (1)

where $K_1$ and $K_2$ are the anisotropy constants. The series Eq. (1) is rapidly converging and $K_1 >> K_2$ for CoPt and FePt $L_1_0$ alloys. The MAE is then computed as the total energy difference when magnetization is oriented along [110] and [001] crystal axes (MAE = $E[110] - E[001]$).

A significant amount of work has been done to calculate this energy difference from first principles, employing the local spin density approximation (LSDA). For the case of CoPt alloy, the fully relativistic Korringa-Kohn-Rostoker (KKR) method yields the MAE of 0.058 meV/f.u., which is very different from results of linear muffin-tin orbitals method (LMTO) calculations in atomic-sphere-approximation (ASA): 2.29 meV, 1.5 meV, and 2 meV, augmented-spherical-wave (ASW) result of 0.97 meV, and full-potential LMTO (FLMTO) calculation results of 1.05 meV and 2.2 meV. As can be seen, there is an apparent and significant scatter of the theoretical results, while the experimental measurements are known to be quite accurate and consistent yielding the MAE of 1 meV. The situation is similar for the case of FePt alloy: the LMTO-ASA calculations yield 3.4 meV, 2.8 meV, 3.5 meV, ASW yields 2.75 meV, and FLMTO 3.9 meV and 2.7 meV, and none of these calculations reproduce the experimental MAE of 1.3 – 1.4 meV for the bulk, and 1 – 1.2 meV for the films (when extrapolated to T=0).

The accurate ab-initio calculation of the MAE in itinerant ferromagnet is a very difficult task due to its notorious sensitivity to numerical details. More importantly, the LSDA (or generalized gradient approximation (GGA)) which is conventionally used in the first-principles theory, lacks proper orbital polarization due to Coulomb correlation effects. In this paper, we wish to clarify the ability of the LSDA theory to reproduce the experimental MAE for CoPt and FePt alloys, when highly accurate full-potential relativistic linearized augmented plane wave method (FP-LAPW) is used for the total energy MAE calculations; (ii) to go beyond LSDA and to investigate the role of electron correlations. We account for the on-site Coulomb correlation effects by using the LSDA+U approach and to show that correlations should be included for both "magnetic" (Fe and Co) and "non-magnetic" (Pt) sites to describe consistently the magnetic ground state properties, such as the MAE and spin and orbital magnetic moments. For the first time, we quantitatively demonstrate a significant and complex character of the intra-atomic Coulomb repulsion contribution to the MAE of itinerant ferromagnet with strongly magnetic 3$d$ and non-magnetic 5$d$-elements.

We start with the conventional LSDA band theoretical method together with the relativistic FP-LAPW method and apply them to perform total energy electronic and magnetic structure calculations for the magnetization fixed along each of [110] and [001] axes, respectively and the MAE. The special k-points method is used for Brillouin Zone integration with the Gaussian smearing of 1 mRy for k-points weighting. For convergence of the total energy differences within desired accuracy (bet-
TABLE I: Magnetic Anisotropy Energy (meV/f.u.) calculated using FP-LAPW method within the LSDA theory.

| Material | Ref. [9] | Ref. [11] | Ref. [10] | Present |
|----------|----------|-----------|-----------|---------|
| CoPt | 0.97 | 2.2 | 1.05 | 1.03 |
| FePt | 2.73 | 3.9 | 2.73 | 2.08 |

Experiment: 0.82 (T = 293 K) [3]; 1.00 (T = 0 K) [13] for CoPt, and a = 7.30 a.u., c = 7.15 a.u. for FePt (here a = 7.30 a.u., c = 7.15 a.u. for FePt) are used [11]. The calculated MAE is shown in Table I, in comparison with recent total energy calculations and experimental results. The present FP-LAPW results are in very good quantitative agreement with ASW results of Oppeneer [8] and FLMTO results of Ravindran [10] and disagree substantially with FLMTO results of Galanakis [11] for the reason which is unclear to us. For CoPt alloy the MAE is calculated in a very good agreement with experimental data, while for FePt our LSDA results (together with those of Refs. [9, 10]) overestimate value of MAE by a factor of two.

Very recently, the electron-electron interaction was shown to play an important role for the MAE in itinerant d and f-electron magnetic materials. Here, we use the LSDA+U method combined with relativistic FP-LAPW basis [19, 20] to account for the intra-site Coulomb repulsion $U$. Minimization of the LSDA+U total energy functional with SOC treated self-consistently [17] generates not only the ground state energy but also one-electron energies and states providing the orbital contribution to the magnetic moment. The basic difference of LSDA+U calculations from the LSDA is its explicit dependence on on-site spin and orbitally resolved occupation matrices. The LSDA+U creates in addition to spin-only dependent LSDA potential, the spin and orbitally dependent on-site “$U$” potential which produces the orbital polarization [21]. Since the LSDA+U method is rarely applied to metals, the appropriate values of intra-atomic repulsion $U$ for Fe, Co and Pt atoms in metals are not known precisely as they are strongly affected by the metallic screening. Here we choose $U_{ud}$ from the range of 1-2 eV, and $U_{sd}$ from the range of 0-1 eV (according to the experimental values for pure metals [22]) in order to reproduce experimental values of the MAE. For the exchange $J$ we use the values of $J_{Co} = 0.911$ eV, $J_{Fe} = 0.844$ eV, $J_{Pt} = 0.544$ eV which are obtained as a result of constrained LSDA calculations [23], and are close to their atomic values.

First, we discuss the FePt alloy. The MAE as a function of $U_{Fe}$ is shown in Fig. 1(a). When $U$ is included on Fe-site only and varied in the interval of 1-2 eV, the MAE is decreasing from its LSDA value. The experimental value of the MAE can not be reached without unreasonable increase of $U$. Further meaningful reduction of the MAE can be achieved by including $U$ on the Pt-site (see, Fig. 1(a)) and for the value of $U_{Pt}$ around 0.544 eV (= $J_{Pt}$) the MAE observed for the bulk FePt can be reproduced. We note that the correct value of the MAE can be obtained in the region of $U_{Fe} \approx 1.5-1.6$ eV, $U_{Pt} \approx 0.5-0.6$ eV.

We choose the $\{U_{Fe} = 1.516$ eV, $U_{Pt} = 0.544$ eV $\}$ as a representative material specific parameters set to analyze the spin and orbital ground state properties. The calculated spin $M_s$, orbital $M_l$ and total magnetic moments for the magnetization directed along [001] axis are shown in Table II. The LSDA+U agrees with observed total magnetization/f.u. $M^{tot}$, yields a slight increase of $M^{Fe}_s$ from its LSDA value of 2.88 $\mu_B$ and substantially increases the $M^{Fe}_l$ from 0.0657 $\mu_B$. The change of $M_s$ and $M_l$ of Pt-site is very small as compared with LSDA. The effect of $U$ on the $M_l$ is seen to be similar to the "orbital polarization correction" of Brooks et al. (LSDA+OP) [10] (see, Table II). This ad-hoc LSDA+OP

![FIG. 1: (color) The MAE vs intra-atomic Coulomb repulsion ($U$) on 3d-site for (a) FePt alloy; (b) CoPt alloy for different values of $U$ on Pt-site. Note, that we use the bulk experimental MAE values \cite{3,4} extrapolated to $T = 0$ K.](image-url)
TABLE II: Spin ($M_s$), Orbital ($M_l$) magnetic moments for 3d and 5d atoms, and Total Magnetic Moment ($M_{tot}$) per formula unit ($\mu_B$); Magnetic Anisotropy Energy (meV/f.u.) as results of LSDA+U calculations for FePt and CoPt alloys. The LSDA+U calculated $M_s$ and $M_l$ values for bcc-Fe and hcp-Co obtained with the same values for $U_{3d}$ and $J_{3d}$ as for Fe- and Co-atoms in FePt and CoPt alloys.

| Alloy   | Method   | $M_{tot}$ | Atom | $M_s$ | $M_l$ |
|---------|----------|-----------|------|-------|-------|
| FePt[001] | LSDA+U  | 1.3       | Fe   | 3.00  | 0.114 |
|         | LSDA+OP | 2.9       | Fe   | 2.89  | 0.110 |
| CoPt[001] | LSDA+U  | 1.0       | Co   | 1.93  | 0.253 |
|         | LSDA+OP | 1.64      | Co   | 1.80  | 0.161 |
| bcc-Fe[001] | LSDA+U  | U_{Fe} = 1.52 eV, $U_{Pt} = 0.54$ eV | Pt   | 0.34  | 0.048 |
|         | LSDA+OP | 2.37      | Fe   | 0.39  | 0.062 |
| hcp-Co[001] | LSDA+U  | U_{Co} = 1.70 eV, $U_{Pt} = 0.54$ eV | Co   | 1.9-2.1 | 0.284 |
|         | LSDA+OP | 2.4       | Co   | 1.93  | 0.090 |
|         | Exp.     | 1.3       | Co   | 1.93  | 0.253 |

The calculated MAE for FePt alloy is in a good quantitative agreement with XMCD results [24]. For the Pt-site, the agreement is not as good. Probably it is caused by the use of the atomic-like sum rules to extract $M_s$ and $M_l$ from XMCD spectra. This procedure is not reliable for Pt due to substantially itinerant character of Pt 5d-electrons. The LSDA+U calculations reproduce consistently the MAE, total, spin and orbital ground state magnetic moments for CoPt alloy (Table II). Both LSDA and LSDA+OP are only partially successful: LSDA yields correct value of MAE but fails for $M_{Co}^l$ and LSDA+OP improves somewhat $M_l$ but does not reproduce the MAE.

To evaluate further the consistency of the LSDA+U results, we performed the LSDA+U calculations for the elementary 3d-ferromagnet bcc-Fe and hcp-Co with the same values of the $U_{3d}$ and $J_{3d}$ as for Fe- and Co-atoms in FePt and CoPt alloys (see, Table II). It is seen that without any further adjustments of parameters the LSDA+U provides very reasonable results for the orbital magnetization in elemental 3d ferromagnet. These results demonstrate that the on-site Coulomb interaction parameters $U_{3d}$ are well transferable in the transitional d-metal systems.

As for the choice of the Coulomb-U for Pt, the challenge lies in correcting the LSDA orbital polarization without harming the exchange splitting which is expected to be well accounted in the LSDA. The choice of $U_{Pt} = 0.5-0.6$ eV looks quite reasonable. Indeed, for the Pt-5d states having almost equal on-site occupations, the choice of $U_{Pt} \approx J_{Pt}$ corresponds to an effective Stoner exchange $I_{LSDA+U} \approx I_{LSDA}$ preserving the LSDA spin polarization. This allows to ensure that the LSDA+U correction contributes entirely to the orbital polarization. The LSDA+U method, while proposed to deal with the problems specific for the localized states, in fact is not limited by this case. This method can be used as soon as on-site Coulomb correlation in the form of the Hubbard model is physically meaningful. The above comparison with available experimental data for the MAE and spin/orbital magnetic moments, and physically reasonable choice of parameters justify the use of on-site LSDA+U correction for the Pt-5d states as the way to correct on-site orbital polarization.

We now discuss the relation between the MAE and the anisotropy of the orbital magnetic moment $\Delta M_l (= M_l || [110] - M_l || [001])$. Bruno [26] showed that in the limit of strong exchange splitting $\Delta_{ex} >> SOC$, the MAE is proportional to $\Delta M_l$. This model predicts the positive MAE of 0.2 meV for CoPt and negative MAE of -2.1 meV for FePt, in disagreement with the total energy calculations and experiment (Table II).

A more general form for MAE was given in Ref. [27]:

$$\text{MAE} \approx -\frac{\xi}{4}(\Delta M_l^\uparrow - \Delta M_l^\downarrow) + \Delta E_T[\uparrow\downarrow"\text{spin-flip}"
$$

where $\xi$ is the SOC constant. The 1st term ($\Delta E_T$) is the
\[ \uparrow \uparrow, \downarrow \downarrow \text{-spins contribution due to the orbital moment } \vec{L}, \text{ and the 2nd term couples the } \uparrow \downarrow \text{-spins and is related to the spin magnetic dipole moment } \vec{M}. \text{ In the limit of SOC } \ll \Delta_{xz}, \text{ the } \Delta E_T \approx -3\xi^2/\Delta_{xz} |Q_{zz}| \text{ is proportional to the difference of quadrupole moments } Q_{zz} \text{ for } z = [110], [001]. \text{ Note, that this } \Delta E_T \text{ form is valid for Fe and Co since their SOC (0.07-0.08 eV) } \ll \Delta_{xz} \text{ (3-4 eV) and can not be used for Pt which has the SOC (0.6 eV) } > \Delta_{xz} \text{ (0.2 eV)} \] 28.

The Eq. 2 gives for the CoPt alloy \( \Delta E_{Co}^L = 1.4 \text{ meV}, \Delta E_{Pt}^L = -0.7 \text{ meV} \) and \( \Delta E_{Co}^{Pf} = 1.9 \text{ meV} \), and for FePt alloy, \( \Delta E_{Pt}^{Pf} = -0.1 \text{ meV}, \Delta E_{Co}^{Pf} = 1.0 \text{ meV}, \) and \( \Delta E_{Pt}^{Pf} = 1.2 \text{ meV} \). Here, large \( \Delta E^{Fe-Co} \) contributions to the MAE naturally originate from the difference in the inter-plane \([xz, yz]\) 3d - 5d and in-plane \([xy]\) 3d - 3d hybridization. Without \( \Delta E_{Pt}^{Pf} \) contribution, the total MAE of 2.7 meV (CoPt) and 2.1 meV (FePt) can be estimated, exceeding substantially the experimental values (cf., Table II). We can only roughly estimate that \( \Delta E_{Pt}^{Pf} \sim -\Delta Q_{zz} = 0.12 \) (CoPt), 0.09 (FePt) provides additional negative MAE contributions which are expected to reduce a total MAE towards the experimental data. Thus, due to the strong Pt-SOC, neither of commonly used MAE parameterizations 26, 27 based on SOC-perturbation theory expansion is valid on the quantitative and do not provide a substitute for the total energy MAE calculations.

Still, it is of interest to apply the Eq. 2 to analyze qualitatively the origin of MAE dependence on \( U \) shown in Fig.1. This analysis shows that LSDA+U MAE vs \( U \) dependence is qualitatively consistent with the Eq. 2, and the change in \( \Delta E_{Pt}^{Pf} \sim \Delta(M_{t}^{L} - M_{t}^{Pf}) \) contributes substantially to the MAE variations with the \( U \). In particular, we find the “coupling” between \( U_{3d} \) and \( \Delta E_{Pt}^{Pf} \) which originates from strong 3d - 5d hybridization, so that tiny \( U_{3d} \)-induced changes in Pt-\( \Delta(M_{t}^{L} - M_{t}^{Pf}) \) produce substantial MAE change due to the strong Pt-SOC. It also explains surprisingly strong MAE dependence on \( U_{Pt} \) (cf., Fig.1), as a variation of \( U_{Pt} \) causes tiny Pt-\( \Delta(M_{t}^{L} - M_{t}^{Pf}) \) change (\( \sim 10^{-3} \mu_B \)) which in turn changes the MAE substantially due to the strong Pt-SOC.

To summarize, accounting for on-site Coulomb correlations beyond what is included in LSDA, and using the LSDA+U method in a very general implementation including SOC we have provided a microscopic theory of the ground state magnetic properties in \( L_{10} \) FePt and CoPt alloys. It is shown by comparison with the experiment that LSDA+U method is capable of describing quantitatively the MAE and orbital magnetization in these alloys with physically reasonable choice of Coulomb-\( U \) parameters. Using the SOC-perturbation theory model we provide interpretation of our numerical results. These results are believed to be important for quantitative microscopic understanding of the large MAE in these materials, and will assist in the development of the next generation magnetic recording devices operating above \( T_{bit}/in^2 \) recording densities.

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[1] D. Weller and A. Mesar, IEEE Trans. Magn., 36, 10 (1999); S. Sun et al., Science 287, 1989 (2000).
[2] S. Chikazumi, Physics of Magnetism (Krieger, Malabar, FL, 1986).
[3] A. Ye, Yermakov and V.V. Maykov, Phys. Met. Metall. 69, 198 (1990) and references therein.
[4] O. A. Ivanov et al., Phys. Met. Metall. 35, 92 (1973).
[5] S. Razee et al., Phys. Rev. Lett. 82, 5369 (1999).
[6] I. V. Solovyev et al., Phys. Rev. B52, 13419 (1995).
[7] A. Sakuma, J. Phys. Soc. Jpn. 63, 3053 (1994).
[8] G.H.O. Daalderop et al., Phys. Rev. B44, 12054 (1991).
[9] P. Oppeeneer, J. Magn. Magh Mater. 188, 275 (1998).
[10] P. Ravindran et al., Phys. Rev. B63, 144409 (2000).
[11] I. Galanakis, M. Alouani and H. Dreysee, Phys. Rev. B 62, 6475 (2000).
[12] J.U. Thiele et al., J. Appl. Phys. 84, 5686 (1998); J.U. Thiele et al., ibid. 91, 6505 (2002); S. Okamoto et al., Phys. Rev. B66, 024413 (2002).
[13] We use E.R. Callen and H.B. Callen theory (J. Phys. Chem. Solids 27, 1271 (1966)) and experimental magnetization \( M(T) \) dependence 3, 4, 11 to find MAE(\( T \rightarrow 0 \)).
[14] J. Trygg et al., Phys. Rev. Lett. 75, 2871 (1995). The numerical convergence of the calculated difference in the total energy was analysed following this work.
[15] I. V. Solovyev, A. I. Liechtenstein, and K. Terakura, Phys. Rev. Lett. 80, 5758 (1998).
[16] V.I. Anisimov, F. Aryasetiawan and A. I. Liechtenstein, J. Phys.: Condens. Matter 9, 767 (1997).
[17] A. B. Shick, D. L. Novikov, and A. J. Freeman, Phys. Rev. B56, R14259 (1997).
[18] I. Yang, S. Savrasov and G. Kotliar, Phys. Rev. Lett. 87, 216405 (2001).
[19] A. B. Shick and W. E. Pickett, Phys. Rev. Lett. 86, 300 (2001).
[20] A. B. Shick, A. I. Liechtenstein, and W. E. Pickett, Phys. Rev. B 60, 10763 (1999).
[21] In these calculations, both \( V_{LSDA} \) and \( V_{+U} \) are determined self-consistently. The charge/spin densities which are needed for the \( V_{LSDA} \) are converged better than 5. \( \times 10^{-5} \) electron/(a.u.)\(^3\) in order to achieve the total energy convergence better than few \( \mu \text{eV} \).
[22] M.M. Steiner, R.C. Alberts and L.J. Sham, Phys. Rev. B 45, 13272 (1992).
[23] I.V. Solovyev, P. H. Dederichs and V.I. Anisimov, Phys. Rev. B 50, 16861 (1994); Note that small variations of \( J \) are found not to affect the results of calculations.
[24] W. Grange et al., Phys. Rev. B362, 1157 (2000).
[25] The XMCD measures the ratio of \( M_s \) and \( M_l \) to the number of holes \( n_d \) in d-shell. To compare with LSDA+U results, the calculated \( n_d^{ex} = 2.845 \) and \( n_d^{cuf} = 2.370 \) were used together with the experimental \( M_s/M_l \) ratios 28.
[26] P. Bruno, Phys. Rev. B 39, 865 (1989).
[27] G. van der Laan, J. Phys.: Cond. Matter 10, 3239 (1998).
[28] A. B. Shick et al., Phys. Rev. B 54, 1610 (1996).
[29] I. Mazin et al., cond-mat/0206548 (2002).