Cu substituted CeCo₅: New optimal permanent magnetic material with reduced criticality

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A comprehensive theoretical prediction using a mechanism of site substitution confirms the crucial role of Cu in enhancing the capabilities of CeCo₅ as a competitive magnet with its known high coercivity. A remarkable enhancement of magnetic anisotropy energy (MAE) of 3.09 meV/f.u. and 2.94 meV/f.u. without significant decrease of magnetic moment is found for 10% and 5% Cu substitution at 2c sites of the hexagonal lattice. Calculations predict the increment of coercivity and magnetocrystalline anisotropy (1.6 times) compared to pristine CeCo₅. The exceptional enhancement in MAE is due to the formation of asymmetric charge hybridization among the Cu (2c) and Co (both 2c and 3g) sites along the uniaxial direction. Because of this asymmetric charge distribution environment, the intrinsic behavior of Ce adjacent to Cu changes abruptly making them more uniaxial and magnetically enhanced creating mixed valence states. For these calculations, we have employed the full-potential augmented plane wave method in conjunction with spin orbit coupling.

1. INTRODUCTION

Superiority of a permanent magnetic material is judged by its high magnetocrystalline anisotropy (MCA) and large magnetic moment. In this context, rare earth (RE) based compounds are considered as the best candidates because of their favorable physical properties and outstanding technological applications.^{1,2,3,4,5} The race for rare earth containing magnets started after the discovery of YCo₅ by US Air Force material laboratory^{6,7} in 1966 which was the material with the largest magnetic anisotropy of that time. Considerably almost all rare earth elements (except promethium, ytterbium, and lutetium) can combine with cobalt to form hexagonal CaCu₅ structure.⁸ However, CeCo₅ is exceptionally peculiar among the RCo₅ class of compounds because of its uniqueness in physical properties. There are anomalous deviations in usual trend of lattice parameter, Curie temperature, and magnetic moment in CeCo₅ within the RCo₅ class of compounds.⁹ Also among all rare earth elements Ce is abundant in nature and is relatively cheaper.

Most of the cerium compounds exhibit mixed valence states with 4f shell occupancy between 0 μ_B (Ce⁴⁺) and 1 μ_B (Ce³⁺). Although the magnetic moment of CeCo₅ is 1.8 μ_B lower and less ferromagnetic than that of YCo₅, its magnetocrystalline anisotropy energy is about 1.46 times higher.⁸ The MAE of a material is defined as the differences between the ground state energies of two magnetic directions. Large anisotropy in the RCo₅ compounds are mainly due to the

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spin-orbit interaction of the partially occupied 4f orbital moment within the rare earth atoms, and the spin-orbit interaction of 3d orbitals within Co atoms caused because of the crystalline environment of the hexagonal lattice.

Additionally, another important quantity called magnetic coercivity in materials is defined as the strength to sustain magnetization of a ferromagnetic material in presence of external magnetic field. Studies^{10,11,12} showed that with the inclusion of Cu in CeCo₅ have tendency to increase the magnetic coercivity in the system. This change in coercivity is because of the transition from Ce⁴⁺ to Ce³⁺ valence state. Earlier works^{11,13} show that Ce in CeCo₅ and CeNi₅ is found to be in the Ce⁴⁺ state, and hence the lattice radius is more quenched compared to the usual trend in RCo₅ compounds. However, the valence state of cerium in CeCu₅ is found to be Ce³⁺. In this manuscript, we performed density functional theory (DFT) calculations and found absurd change in the magnetocrystalline anisotropy in CeCo_{5-x}Cu_x compared to the pure CeCo₅. The variation of Cu composition is tuned by doping at both 2c and 3g sites of Co atoms. The calculations suggest that the MAE is increased by 1.72 times in CeCo_{4.5}Cu_{0.5} as compared to that of CeCo₅.

2. METHODS

The theoretical calculations were performed using the density functional theory (DFT)¹⁴ to study the ground state properties of the pure and Cu substituted CeCo₅. The crystal structure for CeCo₅ and the optimal material with Cu (i.e. for CeCo_{4.5}Cu_{0.5}) are shown in figure-1 where Cu was substituted at the 2c site. The substitution of Cu in hexagonal ring of Co (2c) in the Ce plane showed the maximum magnetic anisotropy for the compound. We employed the full-potential linearized augmented plane wave (FP-LAPW)¹⁵ method within the generalized gradient approximation (GGA), and included the spin orbit coupling (GGA+SOC) to calculate the magnetocrystalline anisotropy for the system. We have also compared the MAE results by the inclusion of the onsite electron correlation parameters U=5.2 eV and J=0.75 eV. It is well known that for light rare earths the U values range from 4 eV to 7 eV without affecting much to the physical properties.¹⁶ The k-space integrations have been performed at least with 13×13×15 Brillouin zone mesh which was sufficient for the convergence of total energies (10⁻⁶Ryd.), charges, and magnetic moments. For RCo₅ systems, the higher values of plane-wave cutoff (RK_{max} = 9.0 and G_{max}=14) are required. Here, magnetocrystalline anisotropy energy (MAE) is calculated using the force method, where difference was taken between c-axis and the planar of the total eigenvalue energies for both spins.

$$MAE \approx \sum_{i=1}^{occupied} \varepsilon_i \vec{a}_{plane} - \sum_{i=1}^{occupied} \varepsilon_i \vec{a}_{z-axis}$$

Where, ϵ is the sum of eigenvalues for both spins in corresponding directions and \vec{a}_{z-axis} and \vec{a}_{planar} are easy and planar directions. The positive (negative) values for the corresponding MAE correspond to the uniaxial and planar anisotropy.

3. RESULTS AND DISCUSSION

CeCo₅ forms in the CaCu₅-type hexagonal structure (P6/mmm) with three non-equivalent sites: Ce (1a), Co (2c) and Co (3g) shown in figure-1(a). The hexagonal ring of Co (2c) sites contains the Ce (1a) in the middle and is sandwiched between the Co (3g) layers. Because of the unique nature of the electronic structure of Ce and its integration in



FIG. 1. Crystal structures for (a) CeCo₅ and (b) CeCo_{4.5}Cu_{0.5} with Cu substituted in the 2c site. Here, Co1 and Co2 represents cobalt positions at 2c and 3g sites, respectively.

the remarkable layered hexagonal crystal structure, $CeCo_5$ leads to the quenching of the 4f orbital moment and hence the magnetic anisotropy becomes uniaxial in the hexagonal environment of $CeCo_5$. For $CeCo_5$, we used the experimental lattice constants as a=4.919 Å and c= 4.029 Å,¹⁷ and the atomic radii for Ce and Co are fixed to 2.5 and 2.19 with force minimization of 3%. The optimized lattice constants remained same as that of experimental values. Although Cu is non-magnetic in nature but it helps in enhancing the coercivity by forming Ce^{3+} state in $CeCu_5$ compared to the Ce^{4+} state in $CeCo_5$ compound.^{9,10} To enhance the magnetic anisotropy in the system without compromising the magnetic moment and coercivity, we introduced the Cu substitution as $CeCo_{5-x}Cu_x$ by varying x= 0.25 to 1.0 in the system. We substituted Cu at 2c and 3g sites of the primitive lattice in corresponding concentrations. The difference in the formation energies between 2c and 3g site substituted compounds is small (i.e. 56.08 meV) indicating a possibility of Cu substitution in both sites. Next, small Cu concentration cell is generated by making the supercell, replacing the 2c and 3g sites of Co with Cu atoms which can be seen in Figure-1(b). In the CaCu₅-type hexagonal structure of CeCo₅, there are two symmetry directions (XY-plane and Z-axis) to create supercell. Here the minimum configuration structure was obtained in the XY-plane, and Cu substitution calculations were performed with $2\times1\times1$ and $2\times2\times1$ supercell. The calculations with different Cu substitution patterns showed negligible effects on the results.

For CeCo₅ Spin polarized calculations with GGA+SOC and GGA+U+SOC resulted to the total magnetic moment of 6.94 $\mu_B/f.u.$ and 7.23 $\mu_B/f.u.$ (6.04/0.90 $\mu_B/f.u.$ and 6.04/1.19 $\mu_B/f.u.$ spin/orbital moments), respectively. The spin and orbital moment contribution of Ce atom within GGA+SOC (GGA+U+SOC) are -0.73 (-0.97) µ_B and 0.27 (0.57) µ_B, respectively. Because of the antiferromagnetic alignment of the spin and orbital moments of the Ce atoms, the overall moment of the system decreases which eventually becomes less than that of YCo5.8 The experimental total magnetic moment and earlier theoretical magnetic moments for CeCo₅ are 7.1 $\mu_B/f.u$,^{18,19} and 6.512 $\mu_B/f.u$,⁸ respectively. Although the inclusion of the onsite correlation²⁰ is important for treating 4fstates, there is only one 4f electron in Ce atom and hence the onsite correlation may not be necessary. The calculations with GGA clearly show magnetic moment that are very close to the experimental value compared to that of GGA+U+SOC. Interestingly the total magnetic moment of $CeCo_5$ is less than YCo_5 (nonlanthanide compound), the magnetocrystalline anisotropy of CeCo₅ is higher than YCo₅.¹⁷ The calculated values for MAE for CeCo₅ is 1.94 meV/f.u. (3.68 MJ/m³) without U which is fairly comparable to the experimentally observed value¹⁸ of 10.5 MJ/m³ (and 1.16 meV/f.u. with the inclusion of U=5.2 eV and J=0.75 eV¹⁹). The substantial difference in computed and experimental values of MAE has also been reported by many authors^{21,22,23} for many systems. We also note here that MAE calculations from DFT are very sensitive to the energy locations of the split 4f states. To verify, MAE we have also employed self-consistent total energy method in which the total energies along the planar and the c-axis magnetization directions are subtracted. The benchmark calculations for GGA+SOC for CeCo₅ give MAE of 1.94 meV/f.u. and 1.85 meV/f.u. using force and energy methods, respectively. The difference in the value of MAE with both methods is negligible.

System	GGA+U		GGA	
	MAE	Total moment	MAE	Total moment
	(meV/f.u.)	$(\mu_B/f.u.)$	(meV/f.u.)	(µ _B /f.u.)
CeCo5	1.16	7.23	1.94	6.94
CeCo _{4.75} Cu _{0.25} (at 2c)	1.62	6.1	2.94	6.15
CeCo _{4.5} Cu _{0.5} (at 2c)	1.99	5.95	3.09	5.84
CeCo _{4.5} Cu _{0.5} (at 3g)	1.26	6.07	2.06	5.96
CeCo ₄ Cu (at 2c)	planar	4.85	planar	4.79
CeCo ₄ Cu (at 3g)	0.01	5.26	0.97	5.13

Table 1: MAE and total magnetic moments for Cu substituted CeCo5 at various concentrations.

The substitution of non-metallic Cu atom with x=0.5 leads to the highest anisotropy in CeCo_{5-x}Cu_x compound. The magnetocrystalline anisotropies with the 2c and 3g site substitutions are 3.09 meV/f.u. (5.86 MJ/m³) and 2.06 meV/f.u. (3.91 MJ/m³), respectively, while the total magnetic moments for the corresponding site substitutions are 5.84 μ_B /f.u. and 5.96

 μ_{B} /f.u. The total spin (orbital) moment contributions are calculated as 5.05 (0.79) μ_{B} /f.u. for the 2c sites substitution and 5.1 (0.85) μ_{B} /f.u. for the 3g sites substitution. Although the low presence of Cu atoms in the unit cell reduces the total magnetic moment only by 15.5% compared to CeCo₅ primitive cell, but it helps in enhancing the MAE of the entire system significantly by 1.6 times higher than the pure CeCo₅ compound. Similarly, for x=0.25 the MAE is calculated as uniaxial with value of 2.94 meV/f.u. Because of less content of Cu in the cell the total magnetic moment is 6.15 μ_{B} /f.u. higher than all other concentrations. The magnetocrystalline anisotropies were completely different for x=1.0 at 2c and 3g sites as compared to that of x=0.5. The anisotropy becomes planar for 2c site substitution, whereas the 3g site substitution small uniaxial MAE of 1.0 meV/f.u. found for CeCo₄Cu compound. In this case, due to the presence of higher Cu concentration in the cell, the total magnetic moment also decreased to 4.79 μ_{B} /f.u. and 5.13 μ_{B} /f.u. for the 2c and 3g site substitutions, respectively.

To investigate this abrupt change of the MAE in $CeCo_5$ going from pure to 5%-20% site substitution with Cu, we analyzed individual magnetic moments, total and partial density of states, and charge density including band structures. Close investigation of Ce atomic moment indicates that the Ce 4f spin and 4f orbital moments are always aligned antiparallel in all



FIG. 2. Density of states at different concentration of x in Cu for $CeCo_{5-x}Cu_x$. Black dot, blue dashed, red, dark green and light green lines correspond to the total (system), Ce (4f), Cu, Co at 2c and Co at 3g sites, respectively.

(pristine and doped) cases. Atomistic spin moment is less negative ($-0.71 \mu_B$), whereas the orbital moments are less positive $(0.26 \ \mu_B)$ in doped systems compared to that of pure CeCo₅ (-0.73 \ \mu_B and 0.27 \ \mu_B). This change hardly affects the total magnetic moment of the doped system, however the total moment of Ce becomes importantly -0.45 $\mu_{\rm B}$ forming a mix valence state between Ce^{4+} and Ce^{3+} . This is also clear from the density of states (DOS) of the corresponding systems shown in Figure 2 and Figure 3. The inclusion of onsite electron correlation parameter shifts (towards lower energy) and sharpens the Ce-4f peak below the Fermi level. For CeCo₅, the spin down DOS shows a sharp peak below the Fermi level contributed by Ce, whereas the peak broadens in the doped cases. This broadening of peaks can be understood by the nature of hybridization within the system when it is substituted by Cu atoms at different sites. The DOS contributed by Cu are far below the Fermi level as compared to the DOS contributed by Co and Ce atoms. Minor overlap of electron density is found around the Fermi level and this is a key point of not lowering down the magnetic moment of the entire system. Figure 3 shows band structures with majority spins (red) and minority spins (blue) of $CeCo_5$ and $CeCo_{4.5}Cu_{0.5}$ (with Cu at 2c site substitution). The metallic nature of the CeCo₅ has been found with less crossover of majority spins compare to the minority spin bands. The majority spins are not affected with substitution. However, because of slightly shifting of bands around the Fermi level, more minority spin crossover is seen for the Cu substituted case. Moreover, the reported results here are obtained from 0 K advanced density functional calculations. As explained above the 5 and 10 percent of Cu substitutions slightly affect the magnetic moment but significantly enhance the magnetic anisotropy field. It is understandable that effective exchange interactions will be slightly reduced while diluting Co atoms by Cu thereby slightly reducing the Curie temperature. The Curie temperature will still be at or above the room temperature with these small substitutions. As pointed out above, the 20 % and more Cu substitutions, however, change the magnetic anisotropy from uniaxial to planar and substantially reduce the magnetic moment.



FIG.3. Band structure plots for CeCo₅ and CeCo_{4.5}Cu_{0.5} (at 2c) around the fermi level using GGA+SOC. Red (blue) lines represent the majority (minority) spin carriers.

Total charge densities for pure and Cu substituted CeCo₅ are shown in figure 4. The asymmetric charge hybridization among the Cu (2c) and Co (2c and 3g) atoms along the uniaxial direction is found. This is the origin of higher MAE in the Cu substituted compounds as compared to that of pure CeCo₅. The charges are uniformly distributed within the crystal lattice in CeCo₅, where the Co atoms at 2c and 3g sites form symmetrically hybridized layers along the z-axis making the valence state of cerium tetravalent. While substituting Co at 2c by Cu [Fig. 4 (b)], the hybridization layers of 2c and 3g are affected resulting a non-uniform charge distribution along the z-axis forming a bilayer of Co and Cu in the system. Because of this asymmetric charge distribution environment, the cerium atoms close to those of Cu atoms become more uniaxial in nature, which is clearly visible in Fig. 4 (b). This leads to the change in the intrinsic behavior of Ce atoms to change abruptly making them more axial and magnetically enhanced. Uniquely distributed charge affects to the magnetic moment of Ce atoms and therefore it gives rise to a mixed valence state between Ce^{4+} and Ce^{3+} with cerium total magnetic moment of -0.45 μ_B within



FIG.4. 2D total charge densities for (a) $CeCo_5$ and (b) $CeCo_{4.5}Cu_{0.5}$. Plots show the asymmetrically hybridized charge layers formation in $CeCo_{4.5}Cu_{0.5}$ making Ce atoms more coaxially aligned near to Cu atoms when placed at 2c sites.

4. CONCLUSIONS

In conclusion, by performing first principles calculations, we have demonstrated a very crucial role of Cu in enhancing the capabilities of $CeCo_5$ as a better magnet with its naturally existing high coercivity. The detailed electronic structure analysis of the site substitution mechanism in the hexagonal $CeCo_5$ crystal shows that the 2c site gives rise to highest uniaxial magnetocrystalline anisotropy energy of 3.09 meV/f.u. and 2.94 meV/f.u. without affecting the total magnetic moment in the system with 10% and 5% Cu substitution, respectively in $CeCo_5$. However, the calculations also suggest that the dense substitution (20% or higher) leads to the planar anisotropy. Layered hybridization of transition atoms found with less Cu content helps in increasing the anisotropy of the system with the formation of mixed Ce valence states.

5. ACKNOWLEDGEMENT

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- ¹ H. R. Kirchmayr and C. A. Poldy, in *Handbook on the Physics and Chemistry of Rare Earths*, edited by K. A.
- Gschneidner, Jr. and L. Eyring (North-Holland, Amsterdam), Vol. 2 (1979) p. 69.
- ² B. Szpunart and P. A. Lindgard, J. Phys. F **9** (1979) L55.
- ³ A. S. Ermolenko, IEEE Trans. Magn. **15** (1979) 1765.
- ⁴ Zhao Tie-song, Jin Han-min, Guo Guang-hua, Han Xiu-feng, and Chen Hong, Phys. Rev. B **43** (1991) 8593.
- ⁵ A. S. Ermolenko, Phys. Met. Metall. **50** (1980) 53.
- ⁶ O. Werner, O. and Strnat Karl J, US Patent 3, **421** (1966)889.
- ⁷ H. Gary, O.John C, O. Werner and S.Karl J, US Patent 3, **540** (1970) 945.
- ⁸ K. H. J. Buschow, Rep. Prog. Phys. **40**, 1179 (1979); in Ferromagnetic Materials, edited by E. P. Wohlfarth (North-Holland, Amsterdam), Vol. **1** (1980) p. 297.
- ⁹ Lars Nordström, Olle Eriksson, M. S. Brooks, and Börje Johnsson, Phys. Rev. B **41** (1990) 9111.
- ¹⁰ E. A. Nesbitt, R. H. Willens, R. C. Sherwood, E. Buehler and J. H. Wernick, Appl. Phys. Lett., **12** (1968) 361.
- ¹¹ E. A. Nesbitt, G. Y. Chin, P. K. Gallagher, R. C. Sherwood and J. H. Wernick, J. Appl. Phys., 41 (1970) 1107.
- ¹² D. Girodin, C.H. Allibert, F. Givord, and L. Lemaire, J. Less-Common Met., **110** (1985) 149-158.
- ¹³ J. H. Wernick, in R. W. Cahn (ed.) *Physical Metallurgy*, North-Holland, Amsterdam (1970) p. 257.
- ¹⁴ P. Hohenberg and W. Kohn, Phys. Rev. 136, B864 (1964); W. Kohn and L. Sham, ibid **140** (1965) A1133.
- ¹⁵ P. Blaha, K. Schwarz, G. Madsen, D. Kvasnicka, and J Luitz, *WIEN2k*, An Augmented Plane Wave + Local Orbitals

Program for Calculating Crystal Properties (Karlheinz Schwarz, Techn. Universität Wien, Austria), ISBN **3-9501031-1-2** (2001).

- ¹⁶ I. L. M. Locht, Y. O. Kvashnin, D. C. M. Rodrigues, M. Pereiro, A. Bergman, L. Bergqvist, A. I. Lichtenstein, M. I. Katsnelson, A. Delin, A. B. Klautau, B. Johansson, I. Di Marco, O. Eriksson Phys. Rev. B **94** (2016) 085137.
- ¹⁷ F. Meyer-Liautaud, S. Derkaoui, C. H. Allibert, and R. Castanet, J. Less-Common Met. **127** (1987) 231.
- ¹⁸ M. I. Bartashevich, T. Goto, R. J. Radwanski, and A. V. Korolyov, J. Magn. Magn. Mater. **131** (1994) 61-66.

- ¹⁹ Liqin Ke, D. A. Kukusta, and Duane D. Johnson, Phys. Rev. B **94** (2016) 144429.
- ²⁰ P. Larson, I. I. Mazin, and D. A. Papaconstantopoulos, Phys. Rev. B **67** (2003) 214405.
- ²¹ L. Nordstrom, M. S. S. Brooks, and B. Johansson, J. Phys.: Condens. Matter **4**, (1992) 3261.
- ²² G. H. O. Daalderop, P. J. Kelly, and M. F. H. Schuurmans, Phys. Rev. B **3**, (1996) 14415.
- ²³ M. Yamaguchi and S. Asano, J. Magn. Magn. Mater. **161** (1997) 168.