Role of antisite disorder, electron-electron correlations, and a surface valence transition in the electronic structure of CeMnNi₄

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CeMnNi₄ exhibits an unusually large spin polarization, but its origin has baffled researchers for more than a decade. We use bulk sensitive hard x-ray photoelectron spectroscopy (HAXPES) and density functional theory based on the Green’s function technique to demonstrate the importance of electron-electron correlations of both the Ni 3d (U_{Ni}) and Mn 3d (U_{Mn}) electrons in explaining the valence band of this multiply correlated material. We show that Mn-Ni antisite disorder as well as U_{Ni} play a crucial role in enhancing its spin polarization: Antisite disorder broadens a Ni 3d minority-spin peak close to the Fermi level (E_F), while an increase in U_{Ni} shifts it toward E_F, both leading to a significant increase of minority-spin states at E_F. Furthermore, the rare occurrence of a valence state transition between the bulk and the surface is demonstrated highlighting the importance of HAXPES in resolving the electronic structure of materials unhindered by surface effects.

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1. INTRODUCTION

In recent years, hard x-ray photoelectron spectroscopy (HAXPES) has turned out to be a reliable tool to study the electronic structure of correlated systems, thin films, and buried interfaces of materials, thus providing new insights into their physical properties [1–3]. In this paper, we present the first study of the electronic structure of CeMnNi₄, an interesting material with large spin transport polarization of 66% [4], using HAXPES and density functional theory (DFT) calculations based on the spin-polarized relativistic Korringa-Kohn-Rostoker (SPRKKR) method [5]. CeMnNi₄ has a cubic MgCu₂Sn-type structure [6]; it is ferromagnetic with a magnetic moment of 4.95 μ_B and Curie temperature of 140 K [4]. These encouraging properties of CeMnNi₄ started a flurry of activity aimed at understanding its electronic structure [7–9]. However, no photoemission study of its electronic structure has been reported to date, and the theoretical studies so far have been unable to explain the different aspects of its electronic structure and its spin polarization in particular. The early DFT calculations [7] reported a spin polarization [10] (P₀) value of about 16–20%; and the much larger experimental polarization was attributed to disorder or nonstoichiometry of the specimens. In fact, in a subsequent x-ray absorption fine structure (XAFS) study, about 6% Mn-Ni antisite disorder was reported [8]. The authors also performed a DFT calculation using the pseudopotential method as implemented in the VASP code, including an ordered antisite defect configuration of nearest-neighbor Ni and Mn that were site exchanged. Thus, in this approach, the effect of randomly disordered antisite defects is not taken into account. Their results, however, showed a significant increase in P₀, which was not related to disorder, but rather to enhanced minority spin states of the site-exchanged Mn 3d partial density of states (PDOS) due to hybridization with neighboring Ni atom [8]. On the other hand, another DFT calculation that considered electron-electron correlation of the Mn 3d electrons (U_{Mn}) but no antisite defect showed that P₀ increases with U_{Mn} [9]. In the absence of any photoemission study and its direct comparison with theory that addresses the influence of both antisite disorder and correlation, their role in determining the electronic structure and spin polarization of CeMnNi₄ has remained an unresolved question until date.

In this paper, we show that both antisite disorder and electron-electron correlations for Ni 3d (U_{Ni}) and Mn 3d (U_{Mn}) electrons have a crucial influence on the bulk electronic structure of CeMnNi₄. In addition, since U_{Ce} is typically taken to be about 7 eV in Ce intermetallics [11], CeMnNi₄ can be regarded as a multiply correlated system, further complicated by the presence of inherent disorder [8]. U_{Ni} and U_{Mn} are responsible for determining the energy positions of the peaks in the valence band (VB) and their optimum values
(\(U_{\text{Mn}} = 4.5\) eV, \(U_{\text{Ni}} = 6.5\) eV) are obtained by the best agreement between theoretically calculated and experimental HAXPES VBs. A surprising result is that the large \(P_0\) of CeMnNi\(_4\) has two origins: the antisite disorder (\(x\)) and \(U_{\text{Ni}}\). The former broadens a minority spin Ni 3d peak close to \(E_F\), while the latter shifts it toward \(E_F\). Thus, in both cases, the minority spin total DOS at \(E_F\left(n_{\uparrow}(E_F)\right)\) increases, while the majority spin total DOS \(n_{\downarrow}(E_F)\) remains essentially unchanged, resulting in a clear enhancement of \(P_0\). The total magnetic moment exhibits contrasting variation: a decrease with \(x\) and an increase with \(U_{\text{Ni}}\). Furthermore, rare occurrence of a valence state transition on the surface of a ternary material is demonstrated: a bulk mixed valent state transforms to a nearly trivalent \(\text{Ce}^{3+}\) state due to the weakened hybridization on the surface. This highlights the importance of HAXPES in resolving the electronic structure of materials unhindered by surface effects.

II. EXPERIMENTAL AND COMPUTATIONAL METHODS

HAXPES measurements were performed at the P09 beamline in PETRA III synchrotron center, Germany, on polycrystalline CeMnNi\(_4\) ingot that was cleaved under ultrahigh vacuum at \(2 \times 10^{-8}\) mbar pressure to expose a fresh surface. The spectra were recorded by using a Phoibos 225 analyzer with 30 eV pass energy at 50 K [12]. Photons were incident on the sample at a grazing angle (10°) and the photoelectrons were collected in the nearly normal emission geometry. The total instrumental resolution (including both source and analyzer contributions), obtained from the least-squares fitting of the Au Fermi edge in electrical contact with the specimen is 0.26 eV. The stoichiometric ingot of CeMnNi\(_4\) was prepared by an arc melting method and characterized for its structure using x-ray diffraction, as discussed in Ref. [4].

The bulk ground-state properties of CeMnNi\(_4\) have been calculated in \(Fm\bar{3}m\) symmetry using the experimental lattice parameter (\(a = 6.9706\) Å) as determined by neutron powder diffraction at 17 K [6]. Disordered Mn-Ni antisite defects have been considered by setting the 16e site occupations to \(1-0.25x\) for Ni\(_{\text{Ni}}\) and 0.25x for Mn\(_{\text{Ni}}\), while the occupancies at the 4c site were set to \(1-x\) for Mn\(_{\text{Mn}}\) and \(x\) for Ni\(_{\text{Mn}}\), where \(X_Z\) refers to an X atom at a Z atom site (\(X, Z = \text{Ni, Mn}\)). Here, \(x\) quantifies the amount of antisite disorder as the fraction of Mn atoms occupying the Ni sites. In this paper, we have varied \(x\) from 0 to 0.12 and the crystal structures are shown in Fig. 1.

Self-consistent band-structure calculations were carried out using fully relativistic SPRKKR method in the atomic sphere approximation [5]. The exchange and correlation effects were incorporated within the generalized gradient approximation framework [13]. The electron-electron correlations have been taken into account as described in the LSDA+U scheme [14]. The parameters of screened on-site Coulomb interaction \(U\) for all the components (\(U_{\text{Ni}}, U_{\text{Mn}}, U_{\text{Ce}}\)) have been varied up to 7 eV, with the exchange interaction \(J\) fixed at 0.8 eV. The static double counting of LSDA+U approach has been corrected using the atomic limit scheme. The angular momentum expansion up to \(l_{\text{max}} = 4\) has been used for each atom. The energy convergence criterion and coherent potential approximation tolerance has been set to \(10^{-5}\) Ry. Brillouin zone integrations were performed on a \(36 \times 36 \times 36\) mesh of \(k\)-points in the irreducible wedge of the Brillouin zone. We have employed Lloyd’s formula, which provides an accurate determination of the Fermi level and density of states [15]. For calculating the angle-integrated VB spectrum, all the PDOS contributions from \(s, p, d,\) and \(f\) states of Ce, Mn, and Ni were multiplied with the corresponding photoemission cross-sections and then added [16,17]. This is multiplied by the Fermi function and convoluted with the instrumental resolution and an energy-dependent lifetime broadening 0.04 x (\(E_p-E_F\)) [18]. Furthermore, to simulate the inelastic background, both Shirley background [19] and an asymmetric background suggested for HAXPES have been used [20].

The Ce 3d core-level spectra were fitted using a least-squares error minimization routine with each peak assigned a Doniach and Šunjić (DS) line shape [21]. This was further convoluted with a Gaussian function of fixed width to represent the instrumental broadening, 0.26 eV and 1.2 eV for HAXPES and XPS, respectively. Since Ni 2p that appears close in binding energy to Ce 3d might contribute to the
intensity in the Ce 3d region, the Ni 2p peaks were also included in the fitting scheme. The whole region including Ni 2p along with the components is shown in Fig. S1 of the Supplemental Material [22]. A total of ten DS line shapes were used: six for Ce 3d comprising the three f^a components for each spin-orbit (s.o.) peak and four for Ni 2p representing the main peak and satellite for both s.o. components. The parameters defining each DS line shape are the intensity, position (Γ), and asymmetry parameter (α). An inelastic background was also included in the fitting scheme [20]. Thus, a total of 35 parameters defined the full spectral shape, including Ce 3d and Ni 2p. However, some reasonable constraints were needed; for example, (i) the lifetime broadening of f^0 for Ce 3d\(_{3/2}\) was constrained to be greater than or equal to f^0 for Ce 3d\(_{5/2}\), (ii) α was kept equal for all Ce 3d DS components, and (iii) for XPS fitting, the satellites of Ni 2p have same width as HAXPES.

A. Valence band of CeMnNi\(_4\)

The HAXPES VB spectrum recorded with 8 keV photon energy at 50 K shows a step (S) close to E\(_F\) at −0.4 eV; peaks at −1.5 (A), −2.2 (B), −3.6 (C), −4.2 (D), −5.2 eV (E), and a weak shoulder at −6 eV (F) [Fig. 2(a)]. To ascertain their origin and study the influence of disorder on the spectral shape, we have calculated the VB spectra in Fig. 2(a) without (red line with open circles, x = 0) and with 6% Mn-Ni antisite disorder (blue dashed line, x = 0.06). The VB spectra are calculated from the partial DOS (PDOS) shown in Fig. 3. Six-percent disorder is considered because a previous XAFS study [8] inferred a disorder of this magnitude on a specimen that was prepared by the same procedure as ours. We find that disorder results in a small but finite broadening of the VB, but it has no effect on the position of the peaks. However, comparison of the calculated HAXPES VB with experiment shows glaring differences: the peaks corresponding to A and B (black arrows) are positioned at higher and lower energies, respectively, and thus their separation (1.6 eV) is significantly larger compared to experiment (0.7 eV). The peak at −5.4 eV (red arrow) is shifted with respect to peak E of the experimental VB, the peak at −3.3 eV (red tick) appears at a dip, while there is no peak in the theory corresponding to F (see the blue dashed arrows). In Fig. 3, DOS calculated with disorder up to x = 0.12 i.e., 12% antisite disorder) shows increased broadening, but the positions of all the peaks remain unchanged.

Thus, it is obvious from the above discussion that disorder is unable to explain the experimental VB. So, we examine the possible role of correlation starting with U\(_{\text{Mn}}\). As U\(_{\text{Mn}}\) is increased, interesting modifications in the −3 to −6 eV region are observed in Fig. 2(a), which are primarily related to the systematic changes in the Mn 3d contribution to the VB [Fig. 2(b), which is calculated from the Mn 3d PDOS shown in Fig. 4]. At U\(_{\text{Mn}}\) = 0, the Mn 3d states are delocalized over 0 to −5 eV with the most intense peak at −3.3 eV. Increase of U\(_{\text{Mn}}\) narrows the Mn 3d PDOS, the peak intensity increases and it shifts by a large amount to lower energies, i.e., away from E\(_F\) e.g., −5.2 eV for U\(_{\text{Mn}}\) = 4.5 eV. The best agreement with experiment in the −3 to −6 eV region is obtained for U\(_{\text{Mn}}\) = 4.5 eV (black line), where the peaks at −3.6, −4.2, −5.2, and −6 eV appear at the same positions as C, D, E, and F, respectively, of the experimental VB, as shown by the blue dashed arrows in Fig. 2(a). The Mn 3d states contribute to the peak E along with Ni 4s states. However, its intensity is relatively less due to smaller photoemission cross section of Mn 3d with respect to Ni 3d at 8 keV [16].

Although U\(_{\text{Mn}}\) = 4.5 eV provides a good agreement for peaks C-F, the positions of the peaks A and B are not well reproduced as these remain unaltered with U\(_{\text{Mn}}\) (Fig. 4). It is evident that A and B originate primarily from Ni 3d states, and so we calculate the VB by introducing U\(_{\text{Ni}}\), with U\(_{\text{Mn}}\) fixed at 4.5 eV. We find that as U\(_{\text{Ni}}\) increases, the peak at −2.6 eV shifts to higher energy, i.e., toward E\(_F\) (blue dashed line) and appears close to the position of peak B for

FIG. 2. (a) The valence band (VB) HAXPES spectra of CeMnNi\(_4\) at 50 K using 8 keV photon energy (black filled circles) compared with the calculated VB spectra for x = 0 (no disorder) and x = 0.06 (6% Mn-Ni antisite disorder). The VBs calculated with different U\(_{\text{Mn}}\) are shown, where x = 0, U\(_{\text{Ni}}\) = U\(_{\text{Ce}}\) = 0 eV. The zero of the horizontal energy scale corresponds to the Fermi level (E\(_F\)). The spectra are staggered along the vertical axis for clarity of presentation, and the zero of the intensity for each spectrum is indicated by the constant spectral region above E\(_F\) (b) Mn 3d contribution to the calculated VB as a function of U\(_{\text{Mn}}\).

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FIG. 3. Spin-polarized (a) total DOS and the PDOS for (b) NiNi 3d, (c) NiMn 3d, (d) MnNi 3d, (e) MnMn 3d, and (f) Ce 4f as a function of Mn-Ni antisite disorder quantified by $x = 0, 0.06$ and 0.12.

$U_{\text{Ni}} = 6.5$ eV (Fig. 5, see Fig. 6 for PDOS). On the other hand, the peak at $-1.1$ eV initially shifts to higher energies and eventually shifts back to lower energy (green dashed line) toward peak A. The separation of these two peaks is lowest (0.8 eV) at $U_{\text{Ni}} = 7$ eV. However, for $U_{\text{Ni}} = 7$ eV, a new peak appears at $-0.7$ eV in disagreement with experiment. Thus, we conclude that the best agreement is observed for $U_{\text{Ni}} = 6.5$ eV, where the positions as well as the separation (0.9 eV) of the calculated peaks agree well with A and B (black dashed arrows in Fig. 5). Note that the peaks in the $-3$ to $-6$ eV region in the total VB are hardly affected by $U_{\text{Ni}}$.

It is to be noted that in Fig. 5, we also consider a value of $U_{\text{Ce}} (=7$ eV) for the Ce 4f electrons that is generally observed in Ce intermetallic compounds [11]. However, $U_{\text{Ce}}$ does not have any discernible effect on the occupied states and the VB, since the Ce 4f peak appears mostly above $E_F$ at 0.9 eV for $U_{\text{Ce}} = 0$ [Fig. 4(e)] and shifts to higher energy (1.2 eV) for $U_{\text{Ce}} = 7$ eV [Fig. 6(a)]. Thus, due to the significant variation of Ni and Mn 3d states with $U_{\text{Ni}}$ and $U_{\text{Mn}}$, respectively, and taking $U_{\text{Ce}}$ from literature [11], we are able to determine the optimum values of $U$ for CeMnNi$_2$ to be $U_{\text{Mn}} = 4.5$ eV, $U_{\text{Ni}} = 6.5$ eV and $U_{\text{Ce}} = 7$ eV (referred henceforth as $U(4.5, 6.5, 7)$).

The partial contributions of the different PDOS to each of the peaks in the total VB for $U(4.5, 6.5, 7)$ as well as the effect

FIG. 4. Spin-polarized total DOS and Ni 3d, Mn 3d, and Ce 4f PDOS as a function of $U_{\text{Mn}}$ with $U_{\text{Ni}} = U_{\text{Ce}} = 0$ and $x = 0$, where for (a) $U_{\text{Mn}} = 0$ eV, (b) $U_{\text{Mn}} = 2$ eV, (c) $U_{\text{Mn}} = 4$ eV, and (d) $U_{\text{Mn}} = 6$ eV.

FIG. 5. The valence band HAXPES spectrum of Fig. 2 (black filled circles) compared with calculated VB spectra as a function of $U_{\text{Ni}}$, with $U_{\text{Mn}} = 4.5$ eV, $U_{\text{Ce}} = 7$ eV and $x = 0$. 

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B. Spin polarization and magnetic moments

We find that the Mn-Ni antisite disorder has an unexpected positive effect on the spin polarization ($P_0$). As shown in Fig. 8(a) and Table I, $P_0$ exhibits a monotonic increase with $x$, reaching a value of 45% (50%) for $x = 0.06 (0.12)$. This is an important result since in half metals and Heusler alloys, a low experimental value of $P_0$ is generally attributed to disorder [23]. To understand the reason for this unusual behavior, we show the spin-polarized total DOS around $E_F$ in Fig. 8(b). A peak in the minority spin DOS close to $E_F$ at $-0.1$ eV progressively broadens and also shifts by a small amount ($\approx 15$ meV) toward $E_F$ resulting in increase of $n_\downarrow(E_F)$ with $x$. On the contrary, the structureless majority spin DOS and consequently $n_\uparrow(E_F)$ remain almost unchanged. Thus, this contrasting behavior of $n_\downarrow(E_F)$ and $n_\uparrow(E_F)$ brings about the increase of $P_0$ with $x$ [Fig. 8(a)]. Table I defines and shows the partial contributions from Ni 3$d$ ($P_{0_{Ni3d}}$), Mn 3$d$ ($P_{0_{Mn3d}}$), and Ce 4$f$ ($P_{0_{Ce4f}}$) PDOS to $P_0$ for different $x$, and we find that $P_0$ increases solely because of $P_{0_{Ni3d}}$. This is also confirmed in Fig. 9, where the peak in the minority spin DOS is clearly dominated by Ni 3$d$ PDOS (black tick).

Turning to the influence of $U$ on $P_0$ [Fig. 8(c)], we find that it increases with $U_{Ni}$ from about 3.8% for $U(4.5,0.7)$ to 45% for $U_{Ni} = 6.5$ eV, i.e., for the optimum $U(4.5,6.5,7)$. This is related to increase of $n_\downarrow(E_F)$ due to a significant shift of the minority spin total DOS peak toward $E_F$ from $-0.2$ eV.
TABLE I. The total spin polarization ($P_0$, also see Fig. 8) and the partial contributions to $P_0$ from the Ni 3$d$ ($P_{\text{Ni}3d}$), Mn 3$d$ ($P_{\text{Mn}3d}$), and Ce 4$f$ ($P_{\text{Ce}4f}$) PDOS, as functions of Mn-Ni antisite disorder ($x$) and Ni 3$d$ electron-electron correlation ($U_{\text{Ni}}$). $P_0$ is calculated using the following formula:

$$P_0 = \frac{|n_\uparrow(E_F)-n_\downarrow(E_F)|}{|n_\uparrow(E_F)+n_\downarrow(E_F)|},$$

where $n_\uparrow(E_F)$ is the majority spin total DOS at $E_F$ and $n_\downarrow(E_F)$ is the minority spin total DOS at $E_F$. The partial contributions to $P_0$ from an Xnl PDOS ($P_{\text{Xnl}}$) where X = Ni, Mn or Ce; $n = 3 - 6$; $l = s, p, d$, or f is given by $P_{\text{Xnl}} = |n_\uparrow(Xnl(E_F))-n_\downarrow(Xnl(E_F))|/|n_\uparrow(E_F)+n_\downarrow(E_F)|$, where $n_\uparrow(Xnl)(E_F)$ is the majority spin Xnl PDOS at $E_F$ and $n_\downarrow(Xnl)(E_F)$ is the minority spin Xnl PDOS at $E_F$. Note that $P_0 = \sum_{X,n,l} P_{\text{Xnl}}$, when all possible X, n, l are considered.

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<th>Mn-Ni antisite disorder</th>
<th>Ni 3$d$ electron-electron correlation</th>
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<td>$x$</td>
<td>$P_0$ (%)</td>
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<td>48.4</td>
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<td>0.12</td>
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FIG. 8. Spin polarization ($P_0$), majority $[n_\uparrow(E_F)]$, and minority $[n_\downarrow(E_F)]$ spin total DOS at $E_F$ (a) as a function of disorder ($x$) with $U_{\text{Ni}} = U_{\text{Mn}} = U_{\text{Ce}} = 0$ and (c) as a function of $U_{\text{Ni}}$, where $U_{\text{Mn}} = 4.5$ eV, $U_{\text{Ce}} = 7$ eV and $x = 0$. Majority and minority spin total DOS around $E_F$ corresponding to (a) and (c) as a function of (b) $x$ and (d) $U_{\text{Ni}}$, respectively.

to $-0.05$ eV [Fig. 8(d)]. Clearly, the total DOS is dominated by Ni 3$d$, black ticks in Fig. 10 show how the minority spin Ni 3$d$ PDOS peak shifts with $U_{\text{Ni}}$. In contrast, the majority spin total DOS is structureless and $n_\uparrow(E_F)$ remains almost unchanged [Figs. 8(c) and 8(d)]. The partial contributions to

FIG. 9. Spin-polarized total, Ni 3$d$, Mn 3$d$, and Ce 4$f$ PDOS in a small range around $E_F$, as a function of antisite disorder (a) $x = 0$, (b) $x = 0.06$, and (c) $x = 0.12$. 

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P₀ for different Uₐ shows that the increase in P₀ is entirely due to P₀.(Table I).

Due to disorder, the Ni 3d minority spin peak will broaden and also possibly shift by a small amount toward Eₐ and thus significantly increase n₁(Eₐ) because of its proximity to Eₐ, e.g., at -0.05 eV for U(4.5,6,6,5,7)). The other hand, n₁(Eₐ) would remain unchanged due to the nearly flat nature of the majority spin total DOS. Thus, disorder would further increase P₀, and assuming that its effect is independent of U, we estimate P₀ for U(4.5,6,6,7,5) to increase from 45% 16% for x = 0.06 (0.12). This is in good agreement with the experimental value of 66%, given the fact that the measurements were performed in the diffusive limit [4] and we calculate the static spin polarization.

We have also studied how Uₐ and Uₐ affect P₀ and find that both have a detrimental effect. In Fig. 11(a), P₀(Uₐ=0,0) shows a decrease from 33.4% to 11.4% with Uₐ varying from 0 to 7 eV. In comparison, the effect of Uₐ is milder with P₀(0,0, Uₐ=0) decreasing from 33.4% to 28%. If Uₐ and Uₐ are set to 0, P₀ increases to a large value of 66% for Uₐ = 7 eV, i.e., for U(0,7,0) [black filled squares in Fig. 11(a)]. On the other hand, a comparison of P₀(Uₐ=0) for (0,Uₐ=0,0), (5,Uₐ=0,0), (4,5,Uₐ=0,7) shows that the extent of increase of P₀ is clearly arrested when Uₐ and Uₐ are nonzero. These results refute an earlier counterintuitive report[9], which concluded that Uₐ increases P₀, while neither Uₐ nor Uₐ have any influence on P₀ (see the Discussion SD1 and Fig. S2) [22].

The calculated magnetic moments show that the total moment of CeMnNi₄ is quite large, e.g., 5.43 μₐ for U(4.5,6,5,7), the main contribution coming from the Mn spin moment (4.31 μₐ). Figure 11(b) shows that both the total moment as well as the Ni spin moment increase with Uₐ, e.g., for U(4.5,0,7) the total moment (Ni spin moment) is 5.15 (0.19) μₐ, whereas for U(4.5,6,5,7) it is 5.43 (0.3) μₐ. The increase in the Ni spin moment is because of the shift of the Ni 3d minority spin states toward Eₐ in Fig.10(d), resulting in a decrease of the integrated occupied minority spin PDOS, while the majority spin PDOS remains largely unchanged. It may be noted that the total moment of 5.43 μₐ for U(4.5,6,5,7) is somewhat overestimated compared to the experimental value of 4.95 μₐ from magnetization measurement at 5 K [4].

Interestingly, we find that the total magnetic moment decreases with increasing disorder [Fig. 11(c)]. This can be ascribed to the difference of the MnNi (Mn atom in Ni position) and MnMn (Mn atom in Mn position) 3d spin-polarized PDOS, the latter having considerably reduced exchange splitting (Fig. 3). This difference is related to the change in hybridization due to different nearest-neighbor configurations.
of a valence state transition, i.e., a change of the valency of Ce between the bulk and the surface. Valence state transition could significantly alter the surface electronic structure compared to the bulk. It was first reported in Sm metal [24], where the top atomic layer had a large divalent component [24]. Subsequently, valence transition has also been observed in binary Ce intermetallic compounds, where the surface has larger 4f occupancy [25].

The Ce 3d core-level spectrum in Fig. 12 displays two sets of triplet peaks corresponding to the s.o. split components. The most intense among the triplet peaks is the $f^1$ satellite associated with a poorly screened $3d^04f^1$ final state occurring at 902.8 eV and 884.4 eV binding energies. The two additional satellite peaks that occur at relatively higher and lower binding energies are referred to as $f^0$ and $f^2$, respectively. The well-screened $f^2$ satellite has an extra screening electron with $3d^04f^2$ final state, while the $f^0$ satellite is related to $3d^04f^0$ final state [26,27]. Notable in Fig. 12 is the large $f^0$ intensity in HAXPES, which decreases drastically in soft x-ray PES (XPS). To extract quantitative information, the Ce 3d core-level spectra were fitted using a least-squares error minimization routine as discussed in the Methods section.

From the least-squares fitting, we find that the normalized intensity of $f^0 (I_n(f^0))$ is 0.15 for HAXPES, where $I_n(f^0) = I(f^0)/\sum_{n=0}^{2} I(f^n)$ (Table II). Such large intensity of $f^0$ having almost similar height as $f^1$ is unusual and has not been observed in other Ce-based intermetallic compounds [28,29]. In contrast, $I_n(f^0)$ is an order of magnitude less (0.04) in XPS. This could be related to the bulk sensitivity of HAXPES with mean free path ($\lambda$) of 91 Å for Ce 3d electrons with $h\nu = 8$ keV, while XPS is surface sensitive with $\lambda = 13$ Å [30] with $h\nu = 1.48$ keV. To understand the differences between the above-discussed bulk and surface Ce 3d spectra, we turn to a simplified version of the Anderson single-impurity model [31] proposed by Imre and Wuijlid (IW), where the extended valence states are considered as a band of infinitely narrow width [11]. The Ce 3d spectrum is calculated as a function of the energy of the unhybridized 4f state relative to $E_F$ ($\epsilon_F$), Coulomb repulsion between 4f electrons at the same site ($U_{ff}$), Coulomb attraction between 4f electron and the final-state core hole ($U_{fc}$), and hybridization between the 4f states and the conduction band ($\Delta$).

The above-mentioned parameters are varied such that the $f^n$ satellites of the calculated Ce 3d$_{3/2}$ spectrum have similar intensities ($I_n$) and energy separations between $f^0$ and $f^n$ ($\delta_{0n}$), as obtained from the fitting of the experimental spectra. For example, besides the large change in $I_n(f^0)$, the binding energies of the $f^n$ satellites are lower in HAXPES, resulting in different $\delta_{0n}$ as shown in Table II. This is not due to recoil effect that is generally observed in light materials, which shifts the spectrum to higher binding energy [1]. The recoil effect, if present causes a uniform shift of the peaks to higher binding energies that increases with the kinetic energy of the electrons, which in turn depends on the photon energy used. We confirm the absence of recoil effect for CeMnNi$_4$ from the Ni 2p spectra taken with different photon energies, where any shift of the peaks for different photon energies is absent (Fig. 13). A satellite feature (black ticks) is observed at 859.4 eV, i.e., about 6.6 eV higher binding energy from the 2p$_{3/2}$ main peak.

C. Surface valence transition

An interesting outcome of our work that emerges from the study of the Ce 3d core-level spectra is the demonstration (Fig. 1). The local moment of MnNi is thus substantially smaller (2.8 $\mu_B$) compared to MnMn (3.8 $\mu_B$). Although the local moments hardly vary, the proportion of MnNi increases with $x$, resulting in a decrease of the total moment. Thus, it can be argued that the overestimation of the total moment by theory with $U(4.5,6.5,7)$ mentioned above could be somewhat compensated by its decrease caused by antisite disorder.
for all photon energies. This can be assigned to the well known 6 eV satellite of Ni metal that arises due to electron-electron correlation in the narrow Ni 3d band [32]. The presence of this satellite feature further confirms the importance of electron-electron correlation in the Ni 3d states of CeMnNi4.

To simulate the HAXPES spectra using IW theory, we note that \( I_n(f^n) \) increases sensitively with \( \epsilon_f \), and so this parameter is varied keeping the others fixed at the values suggested for Ce compounds (\( \Delta = 1.5 \) eV, \( U_{ff} = 7 \) eV, \( U_{fc} = 10 \) eV) [11]. For \( \epsilon_f = -1 \) eV, we find \( I_n(f^0) = 0.15 \) in excellent agreement with experiment; and the other quantities such as \( \Delta_0 \), \( I_n(f^1) \) and \( I_n(f^2) \) are also in good agreement (Table II). The calculated spectrum obtained with \( \epsilon_f = -1 \) eV, \( \Delta = 1.5 \) eV, \( U_{ff} = 7 \) eV, \( U_{fc} = 10 \) eV is shown at the bottom of Fig. 12(a), where the \( f^n \) satellites have been broadened by their respective widths obtained from the fitting. The \( f \) occupancy in the ground state (\( n_f \)) turns out to be 0.8, indicating a mixed valent state with 20% Ce in \( f^0 \) (Ce\(^{4+}\)) while 80% in \( f^1 \) (Ce\(^{3+}\)) configuration.

To simulate the Ce 3d XPS spectrum, we decrease \( \epsilon_f \) to \(-2.5 \) eV from the HAXPES value of \(-1 \) eV and obtain \( I_n(f^0) = 0.04 \). But concomitantly, both \( \delta_{01} \) (\( = 12.1 \) eV) and \( \delta_{02} \) (\( = 18.9 \) eV) become larger than experimental values of 10.2 eV and 14.4 eV, respectively (Table II). To decrease \( \delta_{0n} \), both \( \Delta \) and \( U_{fc} \) need to be decreased, and thus, we obtain a good agreement with experiment for \( \epsilon_f = -2.5 \) eV, \( \Delta = 1.1 \) eV, \( U_{fc} = 8 \) eV, and \( U_{ff} = 7 \) eV [bottom of Fig. 12(b)]. Due to the decrease of \( \epsilon_f \), \( n_f \) increases to 0.98, and thus, in contrast to bulk, at the surface Ce has predominantly 3d\(^0\)f\(^1\) (Ce\(^{3+}\)) ground state. Thus, in the bulk, since \( \epsilon_f = -1 \) eV is closer to \( E_F \) and \( \Delta \) is larger, the Ce 4f electron transfers to the valence states comprising of primarily Ni 3d states, making CeMnNi4 a mixed valent system with 4f occupancy of \( n_f = 0.8 \). However, at the surface, the reduced hybridization between the Ce 4f and unsaturated 3d states results in a lowering of the Ce 4f states further below \( E_F \). This increases the occupancy of the Ce 4f level (\( n_f = 0.98 \)) and results in the surface valence transition. Decrease in \( U_{fc} \) from about \( 10 \) eV to \( 8 \) eV at the surface is also a manifestation of this transition possibly caused by the more efficient screening of the core hole due to increased \( n_f \). Finally, although the valence transition manifests clearly in Ce 3d XPS spectrum, it does not, however, result in the appearance of any Ce 4f peak in the XPS VB because of largely diminished Ce 4f PDOS compared to Ni 3d PDOS in the occupied region as well as lower photoemission cross section of Ce 4f compared to Ni 3d (see Discussion SD2 and Fig. S3) [22].

### III. CONCLUSION

In conclusion, we settle the long-standing debate about the electronic structure of CeMnNi4. We establish the importance of both antisite disorder and electron-electron correlation in explaining its intriguing properties. Our work fundamentally alters the general notion that antisite disorder is detrimental for spin polarization. We hope it will motivate further experimental work on CeMnNi4 and related materials, mainly because disorder could be controlled and \( P_0 \) further enhanced. We find that the total magnetic moment exhibits contrasting behavior, it decreases with \( x \), but increases with \( U_{Ni} \). A valence state transition that originates due to the weakened hybridization on the surface is demonstrated. Our study highlights the power of HAXPES in combination with DFT for clarifying the electronic structure and properties of multiply correlated materials with inherent antisite disorder.
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[10] $P_{0} = \frac{\left| n_{1}(E_F) - n_{1}(E_F) \right|}{\left| n_{1}(E_F) + n_{1}(E_F) \right|}$.


