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## Crucial role of $d$ - $d$ Coulomb correlations in the magnetocaloric ferrimagnets $\text{Gd}_6(\text{Mn}_{1-x}\text{M}_x)_{23}$ ( $M = \text{Fe}, \text{Co}$ )

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It is well-known that in elemental metals, the onsite Coulomb energy of transition-metal (TM)  $d$ -electrons,  $U_{dd}$ , is significantly smaller than  $U_{ff}$  of  $f$ -electron rare-earth (RE) metals. Consequently,  $U_{dd}$  is often neglected in RE-TM intermetallic alloys. In spite of the low value of  $U_{dd}$  compared to  $U_{ff}$ , we quantify and clarify the important role of  $U_{dd}$  in partially filled  $d$ -bands of RE-TM alloys. We investigate the electronic structure of a typical RE-TM ferrimagnetic series  $\text{Gd}_6(\text{Mn}_{1-x}\text{M}_x)_{23}$  ( $M = \text{Fe}, \text{Co}; x = 0.0, 0.3$ ), which shows promising magnetocaloric properties. Resonant photoemission and constant initial state spectroscopy is used to identify the Mn  $3d$ , Fe  $3d$ , and Co  $3d$  partial density of states (PDOS) in the valence band. The photon energy-dependent spectral evolution allows us to separate out the lower Hubbard band and the two-hole correlation satellites in the Mn, Fe, and Co  $3d$  PDOS. Using the Cini-Sawatzky method, we determine an average  $U_{dd} = 2.1 \pm 0.4$  eV,  $2.2 \pm 0.4$  eV, and  $2.9 \pm 0.4$  eV for the Mn  $3d$ , Fe  $3d$ , and Co  $3d$  states, respectively. The relatively larger  $U_{dd}$  for Co compared to Fe  $3d$  states results in lower DOS for the coherent feature at the Fermi level ( $E_F$ ) and higher DOS in the lower Hubbard band away from  $E_F$  in  $\text{Gd}_6(\text{Mn}_{0.7}\text{Co}_{0.3})_{23}$  compared to  $\text{Gd}_6(\text{Mn}_{0.7}\text{Fe}_{0.3})_{23}$ . To understand the role of Coulomb correlations on the electronic structure and magnetic properties, *ab initio* electronic structure calculations using density functional theory with onsite Coulomb correlations (DFT+ $U$ ) were carried out for the parent  $\text{Gd}_6\text{Mn}_{23}$ . The results show that the calculated Mn magnetic moments are consistent with experiments when  $U_{\text{Mn}}^{\text{DFT}} = 0.75$  eV, corresponding to  $U_{dd} = 1.65$  eV and  $J_{dd} = 0.9$  eV. Further, using the calculated Gd and Mn PDOS and known photoionization cross-sections, the simulated  $\text{Gd}_6\text{Mn}_{23}$  spectrum is fairly consistent with the experimental valence band spectrum. The results indicate the crucial role of  $d$ - $d$  correlations in the presence of large  $f$ - $f$  correlations for tuning the electronic structure and magnetic properties of RE-TM intermetallics.

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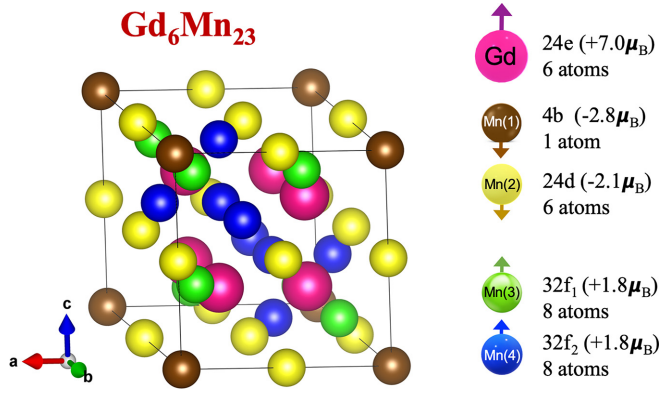
### I. INTRODUCTION

Intermetallic alloys containing rare earths (RE) and transition metals (TM) have played a central role in the fields of heavy-fermions [1–3], non-Fermi-liquids [4], magnetic metals [2–6], magnetocaloric materials [7,8], etc. More recently, there is a resurgence of interest in RE-TM-based materials as they are increasingly used in phosphors, lasers, energy storage batteries, catalysts, etc., in addition to their use as permanent magnets, such as the well-known Nd-Fe-B and Sm-Co alloys [9].

The large variety of applications of RE-TM-based materials arise from the synergy between localized  $f$  electrons of REs and the delocalized  $d$  electrons of TMs. The localized  $f$  electrons exhibit large magnetic moments  $\mu$  and spin-orbit coupling (SOC), negligible bandwidths ( $W$ ), and weak intersite exchange ( $J$ ) interactions [5,6]. In contrast, the delocalized  $d$ -electrons in intermetallics show a smaller  $\mu$  and SOC, but larger  $W$  and  $J$  which determine the magnetic ordering temperature. In an isostructural RE-TM series, with RE varying from Ce-Yb for the same TM, the RE-TM exchange coupling is always ferromagnetic (FM) for light REs

and antiferromagnetic (AFM) for heavy REs, but varying TM can also result in a competition of FM versus AFM order [10,11]. Many studies have carried out first-principles local spin-density approximation electronic structure calculations, without and with onsite Coulomb energy (LSDA and LSDA +  $U$ , where  $U$  is the onsite Coulomb energy) [12–19] as well as dynamic-mean-field theory (DMFT) calculations for understanding the magnetism of RE-TM alloys [20].

Early electronic structure calculations on RE-TM intermetallics focused on only including  $U_{ff}$  and neglected  $U_{dd}$  [12–15,20]. However, a few recent calculations have employed  $U_{ff}$  and  $U_{dd}$  to understand material properties, such as  $d$ -electron correlations in Ce-skutterudites [16], maximal magnetization in  $\text{SmCo}_{5-x}\text{Ni}_x$  [17], and high-spin polarization in  $\text{CeMnNi}_4$  [18,19]. An early pioneering experimental study combining photoemission spectroscopy (PES) and inverse-PES (I-PES; also called bremsstrahlung isochromat spectroscopy) of the  $4f$  RE metals showed that  $U_{ff}$  is large, varying from  $\sim 6 \pm 1$  eV for Ce to Pm, to a maximum of  $\sim 11 \pm 1$  eV for Eu and Gd, and then reduced again to  $\sim 6 \pm 1$  eV for Tb to Yb [21]. A recent experimental study identified the role of  $d$ -electron correlations in the RE-TM

FIG. 1. The cubic crystal structure of  $\text{Gd}_6\text{Mn}_{23}$ 

mixed-valence system  $\text{YbFe}_2\text{Al}_{10}$  [22], although it was not quantified. Empirical formulas have been obtained for  $U_{ff}$  in RE metals because the experimentally obtained values are significantly smaller (due to solid-state screening) than  $U_{ff}$  values obtained from atomic calculations [23]. Similarly, empirical formulas as well as calculations for the elemental 3d TMs showed  $U_{dd}$  varying from  $\sim 1$ –3 eV for Ti to Ni [23,24]. These have been confirmed for the elemental TMs Mn–Ni by comparing LDA/LSDA+DMFT calculations with angle-resolved (AR)-PES experiments and are consistent with measurements of the two-hole final state Auger spectra which provide experimental estimates of  $U_{dd}$  [25–28]. More recently, since the discovery of superconductivity in the iron pnictides, the importance of strong correlations in metallic magnetic materials based on TMs has become well accepted [29–33]. Surprisingly, in spite of extensive studies, to date, there are no estimates of  $U_{dd}$  using the known experimental Cini-Sawatzky method [34–37] to quantify  $U_{dd}$  in RE-TM intermetallics. Since the localization-delocalization and magnetic properties arise from Coulomb and exchange correlations, we felt it is important to experimentally quantify element-specific onsite Coulomb correlations  $U_{dd}$  in the series  $\text{Gd}_6(\text{Mn}_{1-x}\text{M}_x)_{23}$  ( $\text{M} = \text{Fe}, \text{Co}$ ).

The intermetallic compounds  $\text{RE}_6\text{Mn}_{23}$  exhibits the  $\text{Th}_6\text{Mn}_{23}$  type cubic crystal structure (Fig. 1) and show interesting magnetic properties [38–45]. The  $\text{RE}_6\text{Mn}_{23}$  materials show a complex magnetic structure which was solved by polarized neutron diffraction studies of isostructural  $\text{Y}_6\text{Mn}_{23}$ . Delapalme *et al.* showed that the magnetic moments of Mn atoms on the  $b$  ( $\sim -2.8\mu_B$ ) and  $d$  sites ( $\sim -2.1\mu_B$ ) are oriented antiparallel to the moments of the  $f_1$  ( $\sim +1.8\mu_B$ ) and  $f_2$  ( $\sim +1.8\mu_B$ ) sites [42]. Thus, there are two types of Mn spin sites: up-spin “ $f_1$ ,  $f_2$ ” sites, and down-spin “ $b$ ,  $d$ ” sites in  $\text{Y}_6\text{Mn}_{23}$ . Applying the same Mn sublattice structure to  $\text{Gd}_6\text{Mn}_{23}$  in combination with magnetization measurements, it was shown that the localized  $\text{Gd}^{3+}$  spins are oriented parallel to the net Mn sublattice moments [42,46]. For Mn, as well as Fe and Co upon substitution, the magnetic moments indicate a high spin configuration which in turn suggests a small crystal field splitting and a larger exchange interaction [38–45]. More recently, the  $\text{Gd}_6(\text{Mn}_{1-x}\text{M}_x)_{23}$  series has attracted attention for their magnetocaloric properties [46–49,54]. It is also known that the ferrimagnetic Curie temperature  $T_C$  and the bulk magnetization reduce upon

increasing the M content from  $x = 0.0$  to 0.3 [41,44–47]. For  $x = 0.0$ ,  $T_C = 489$  K and it reduces to  $T_C \sim 120$  K for  $x = 0.3$  for both Fe and Co substitutions. A similar behavior is also seen in  $\text{Y}_6(\text{Mn}_{1-x}\text{Fe}_x)_{23}$  [40,44,55,56] and suggests that  $T_C$ 's of  $\text{Gd}_6(\text{Mn}_{1-x}\text{M}_x)_{23}$  originate from the TM-sublattice. Magnetocaloric studies of  $\text{Gd}_6\text{Mn}_{23}$  revealed two maxima in the magnetic entropy changes ( $\Delta S_M$ ), a weaker maxima at  $T = T_C$  and a stronger maxima at  $T \sim 100$  K. The lower  $T \sim 100$  K maxima increased with  $x$  and it was inferred that it could be due to Gd sublattice ordering or due to modifications in the magnetic structure for small  $x = 0.0$ –0.2 [47–49]. More importantly, the cooling or refrigeration capacity  $Q$  for  $x = 0.2$  is significantly high at  $3.4 \text{ J/cm}^3$  for  $\Delta T = 10$ –300 K with a magnetic field variation  $\Delta H = 5$  T [47–49]. In comparison, the original giant magnetocaloric system  $\text{Gd}_5\text{Si}_2\text{Ge}_2$  [57] shows a  $Q = 3.6 \text{ J/cm}^3$  but for a  $\Delta T = 50$  K around  $T_C$  with  $\Delta H = 5$  T. It was thus suggested that  $\text{Gd}_6(\text{Mn}_{1-x}\text{Fe}_x)_{23}$  could be more suited for gas liquefaction applications [47–49].

In this work, we have carried out synchrotron induced resonant PES (RES-PES) and constant initial state (CIS) spectroscopy to identify the PDOS of Mn, Fe, and Co in the valence band of  $\text{Gd}_6(\text{Mn}_{1-x}\text{M}_x)_{23}$  ( $\text{M} = \text{Fe}, \text{Co}; x = 0.0$ –0.3). We observe two-hole satellites which evolve from a resonant Raman satellite (RRS) to a normal Auger feature. This allows us to use the Cini-Sawatzky method [34–37] to estimate the average onsite Coulomb correlation energy  $U_{dd}$  for the Mn, Fe, and Co 3d PDOS. We obtain  $U_{dd} = 2.1 \pm 0.4 \text{ eV}$ ,  $2.2 \pm 0.4 \text{ eV}$ , and  $2.9 \pm 0.4 \text{ eV}$  for the Mn, Fe, and Co 3d states, respectively. In addition, based on the similarity of the 4f spectral feature in the valence band with known results of Gd metal, we estimate  $U_{ff} \sim 11 \text{ eV}$  in the Gd 4f states [21,23]. The results show the importance of  $d$ - $d$  correlations on the electronic structure and properties of  $\text{Gd}_6(\text{Mn}_{1-x}\text{M}_x)_{23}$ , and provide a quantification of average onsite  $U_{dd}$  for use in the theoretical calculations which have not been reported for this series.

## II. METHODS

### A. Sample preparation and characterization

The  $\text{Gd}_6(\text{Mn}_{1-x}\text{M}_x)_{23}$  with  $\text{M} = \text{Fe}, \text{Co}$  and  $x = 0.0$  and 0.3, were synthesized using stoichiometric amounts of high-purity metals (Gd 99.9 wt.% from Rhodia, Mn 99.99 wt.% and Co 99.8 wt.% from Cerac, and Fe 99.8 wt.% from Alfa Aesar) by melting them in a high-frequency induction furnace (CELES) under pure argon atmosphere. The crystal structure was verified to be cubic by powder x-ray diffraction (Fig. 1), using a Philips X-Pert Pro Diffractometer,  $\text{Cu K}\alpha$  [47–49], and it confirmed the absence of impurity phases. The parent material  $\text{Gd}_6\text{Mn}_{23}$  showed a lattice parameter  $a = 12.533(1)\text{Å}$ , which decreased to  $a = 12.335(1)\text{Å}$  for  $\text{Gd}_6(\text{Mn}_{0.7}\text{Fe}_{0.3})_{23}$  and  $a = 12.197(1)\text{Å}$  for  $\text{Gd}_6(\text{Mn}_{0.7}\text{Co}_{0.3})_{23}$ , as reported earlier [47–49]. The chemical purity and composition of each sample was checked by microprobe analysis (Cameca SX100) on mirror polished powder samples dispersed in a cold resin. The microprobe measurements indicate that, within the error bars (ca. 1 at%), the compositions of the alloys, taken from an average of six randomly chosen pinpoints, are homogeneous and identical to their nominal compositions.

### B. Spectroscopy experiments

The soft-x-ray PES and CIS experiments were carried out at BL24A of the Taiwan Light Source using a linearly polarized photon beam with incident photon energies in the range of  $h\nu = 600\text{--}1000$  eV. A liquid-N<sub>2</sub> flow-type cryostat was used to cool the samples down to  $T = 140$  K. Samples were scraped in vacuum preparation chamber at  $1 \times 10^{-7}$  mbar, and immediately transferred to the connected main chamber at a ultrahigh vacuum of  $8 \times 10^{-10}$  mbar for measurements. The energy calibration and resolution ( $\Delta E = 0.5$  eV at  $h\nu = 1000$  eV) were determined from the Fermi edge ( $E_F$ ) spectrum of a gold foil mounted on the sample holder. XAS measurements were carried out using the total electron yield mode (TEY). RES-PES spectra were measured across the Mn  $2p\text{-}3d$ , Fe  $2p\text{-}3d$  and Co  $2d\text{-}3d$  thresholds, and the spectra were normalized for scan time and incident photon flux. The hard x-ray PES (HAXPES) experiments were carried out at the Taiwan beam line BL12XU in SPring-8, Hyogo, Japan, with a total-energy resolution of 0.28 eV using linearly polarized photons. The sample was cooled using a liquid-N<sub>2</sub> flow-type cryostat. Samples were cleaved in the preparation chamber in a vacuum of  $5 \times 10^{-9}$  mbar and immediately transferred for measurements in the main chamber at  $T = 80$  K at a vacuum of  $5 \times 10^{-10}$  mbar. The energy calibration and resolution were determined from the  $E_F$  spectrum of a gold film mounted on the sample holder. The HAXPES data were obtained in the angle-integrated mode with an incident photon energy  $h\nu = 6.5$  keV. The surface contamination was monitored by O  $1s$  and C  $1s$  and the surfaces were clean and stable for 6 h for soft x-ray PES and more than 24 h for the HAXPES measurements. The TM  $2p$  core-level spectra of Fe, Mn, and Co were analyzed using a least-squares fitting method to quantify peak-energy positions, shape and widths. A Shirley-type background with asymmetric Doniach-Sunjić (DS)-type Voigt profiles was found to be appropriate for all measured peaks reported in this study.

### C. DFT+*U* electronic structure calculations

Electronic structure calculations were carried out for the parent Gd<sub>6</sub>Mn<sub>23</sub> using the Vienna ab-initio simulation package (VASP) [50–52] to obtain the PDOS and magnetic moments. The spin-polarized calculations were performed with the projector augmented wave (PAW) method using a plane-wave basis set [52]. We used the following electron configurations:  $3p^6 3d^6 4s^1$  for Mn, and  $5s^2 6s^2 5p^6 5d^1 4f^7$  for Gd. A structural optimization was performed within the GGA-PBE (Perdew-Burke-Ernzerhof) approximation which provided a cubic cell parameter  $a$  close to the experimental value:  $a_{\text{exp}} = 12.54$  Å and  $a_{\text{cal}} = 11.78$  Å. The calculations were performed for the optimized structure using the simplified (rotationally invariant) method to the DFT+*U* [53]. In this method, the onsite Coulomb ( $U$ ) and Hund's exchange ( $J$ ) interactions do not enter separately but only as a single parameter  $U^{\text{DFT}} = U - J$ . The parameters  $U_{\text{Mn}}^{\text{DFT}}$  was varied between 0.0 and 2.3 eV, while for Gd,  $U_{\text{Gd}}^{\text{DFT}}$  was varied from 6.0 to 12.0 eV to obtain magnetic moments close to the experimental values. The one-electron Kohn-Sham orbitals were expanded in a plane-wave basis set and the cutoff for the kinetic energy was 360 eV. The total energies were minimized

until the energy differences between two electronic cycles were less than  $10^{-4}$  eV. The reciprocal space integration was carried out with a Monkhorst-Pack k-point grid of  $9 \times 9 \times 9$ .

## III. RESULTS AND DISCUSSIONS

### A. Two-hole correlations and Mn $3d$ Hubbard band of Gd<sub>6</sub>Mn<sub>23</sub>

The results of Mn  $L$ -edge XAS, off- and on-resonant PES, and the CIS spectra, core-level and valence band PES of the parent material Gd<sub>6</sub>Mn<sub>23</sub> are shown in Figs. 2(a)–2(f). To carry out resonant PES data shown in Figs. 2(b) and 2(c), we first measured the Mn  $L$ -edge XAS spectrum shown in Fig. 2(a). The spectrum shows typical single peak features for the  $L_3$  and  $L_2$  edges at photon energies of  $h\nu = 639.8$  eV and 651.1 eV, respectively, which match well with Mn metal spectrum [28]. The Mn metal type spectra was also confirmed by measuring the Mn  $2p$  soft x-ray PES with a photon energy  $h\nu = 1000$  eV as shown in Fig. 2(d). The Mn  $2p$  spectrum consists of the  $2p_{3/2}$  and  $2p_{1/2}$  features at a binding energy (BE) of 638.4 and 649.7 eV. The Mn  $2p_{3/2}$  and  $2p_{1/2}$  features could be resolved into doublets and fitted with asymmetric Doniach-Sunjić line shapes, consistent with HAXPES results reported recently [58]. It was shown that the relative intensity of the doublets follows the Mn up-spin and down spin site occupancies which change systematically with Fe content  $x$  in Gd<sub>6</sub>(Mn<sub>1-x</sub>Fe<sub>x</sub>)<sub>23</sub>. We then measured the soft x-ray PES valence band [Fig. 2(e)] to characterize the energy range of the valence band features. The valence band spectra show the Gd  $4f$  main peak at about 7.7 eV BE and a weak shoulder at  $\sim 8.8$  eV which is attributed to surface feature as it is missing in HAXPES spectra shown in Fig. 4(c). Two additional features are observed, one at 0.5 eV BE which cuts the  $E_F$  and a broad feature with a peak at 2.7 eV BE. To establish that the 0.5 and 2.7 eV BE features originate from Mn, we measured the CIS spectra at 0.5 and 2.7 eV BE for  $h\nu$  scanning across the Mn  $L$ -edge. The CIS spectra match well with the XAS Mn  $L$ -edge spectra as shown in Fig. 2(a) and confirm their Mn  $3d$  character. The weaker intensity in the 0.5 eV CIS spectra is attributed to the admixture of Gd  $5d$  states at and near  $E_F$ , as was discussed in HAXPES studies [58].

We then selected photon energies labeled A–I as shown in Fig. 2(a), and carried out valence band PES to investigate the Mn  $2p\text{-}3d$  RES-PES behavior [Fig. 2(b)]. Focussing on the spectral features between  $E_F$  and 8.5 eV BE (just beyond the  $4f$  peak), we observe systematic changes as a function of  $h\nu$ . As we increase  $h\nu$  from A to E ( $h\nu = 635.0$  to 638.3 eV) across the Mn  $L_3$ -edge threshold, we observe a systematic increase of the feature at 0.5 eV BE and a stronger increase of the feature at 3.3 eV BE [red dotted line in Fig. 2(b)] due to the Mn  $2p\text{-}3d$  resonance effect. Furthermore, above incident  $h\nu > 638.3$  eV, the high intensity feature at 3.3 eV BE moves to higher BEs (red full line). From photon energies F–I ( $h\nu = 638.8$  eV to 642.8 eV), it systematically shifts to higher BEs from 3.7 to 7.8 eV BE. Since this feature tracks the changes in the photon energy, it arises from a two-hole correlation Auger satellite. To carefully determine the energy positions of this Auger feature, we plotted the difference spectra with respect to the off-resonant PES spectrum measured at  $h\nu = 635$  eV, as shown in Fig. 2(c). The change in BE of this

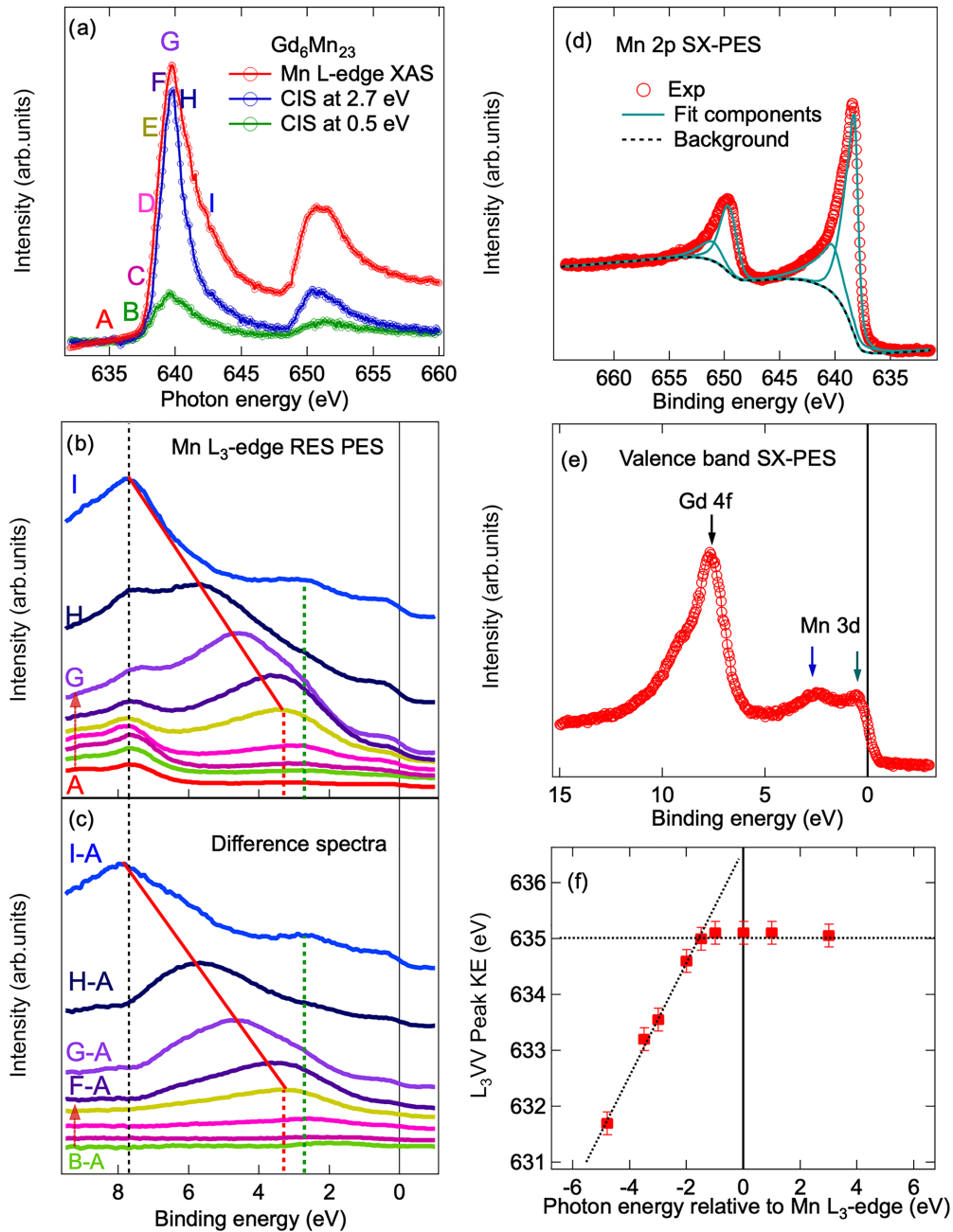


FIG. 2. (a) The Mn L-edge XAS and CIS spectra of  $Gd_6Mn_{23}$ . (b) Mn  $2p$ - $3d$  Res-PES spectra of  $Gd_6Mn_{23}$ . (c) Mn  $2p$ - $3d$  Res-PES difference spectra of  $Gd_6Mn_{23}$ . (d) The Mn  $2p$  core-level SX-PES spectra of  $Gd_6Mn_{23}$  with photon energy  $h\nu = 1000$  eV. (e) The valence band spectra of  $Gd_6Mn_{23}$  with  $h\nu = 1000$  eV. (f) The plot of kinetic energy (KE) of the Auger  $L_3VV$  peak versus the incident  $h\nu$  relative to the Mn L-edge XAS maximum energy. The intersection point of the two dotted straight lines corresponds to the crossover energy of the resonant Raman to normal Auger regime.

feature as a function of incident  $h\nu$  with respect to the XAS main peak energy are plotted in Fig. 2(f). It confirms the two-hole correlation satellite exhibits a RRS to a normal Auger transition, i.e., it corresponds to the  $L_3VV$  Auger feature of Mn  $3d$  character in the valence band DOS. This behavior matches well with Mn  $2p$ - $3d$  Res-PES of Mn metal which also showed a resonance at 3.3 eV BE [28].

Another important point to note is that at the highest photon energy shown in Fig. 2(b), the Mn  $3d$  PDOS shows a broad feature spread between 1.5 and 3.5 eV, with a maximum at  $\sim 2.7$  eV (green dotted line), i.e., 0.6 eV below

the  $L_3VV$  Auger feature at 3.3 eV BE, just as is also seen in Fig. 2(e). This matches well with the lower Hubbard band of Mn metal reported earlier by Biermann *et al.* [25]. The authors carried out AR-PES of Mn metal for  $h\nu = 14$ – $70$  eV and showed that the  $\sim 2.7$  eV BE feature is dispersionless and matches with the lower Hubbard band by comparing with LDA+DMFT electronic structure calculations. They also showed that the coherent quasiparticle feature was positioned within 0.5 eV BE. Thus, our results match closely with the coherent feature at 0.6 eV BE, the lower Hubbard band at  $\sim 2.7$  eV BE and the  $L_3VV$  Auger feature at 3.3 eV BE for Mn

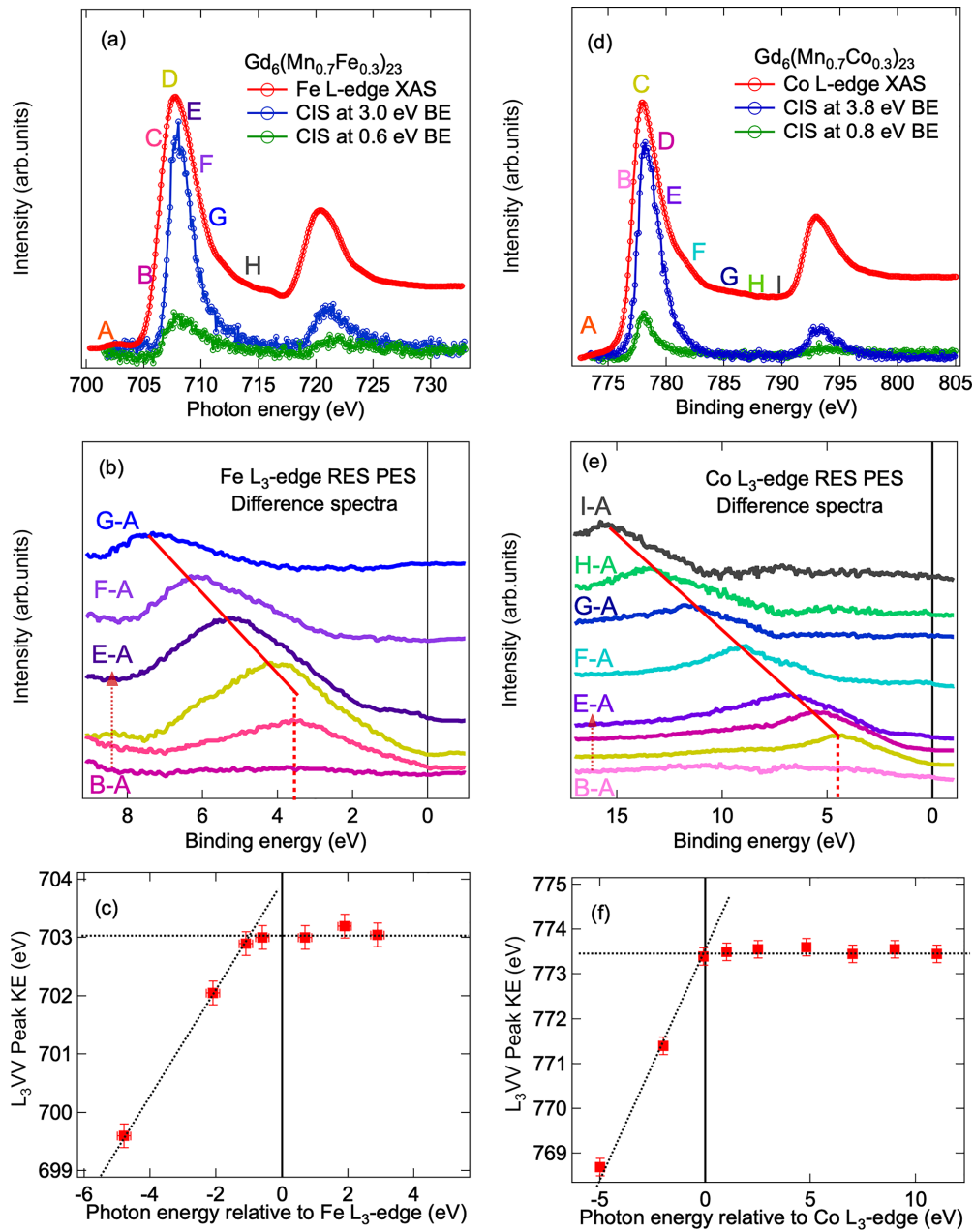


FIG. 3. (a) The Fe L-edge XAS and CIS spectra of  $Gd_6(Mn_{0.7}Fe_{0.3})_{23}$ . (b) Fe  $2p - 3d$  Res-PES difference spectra of  $Gd_6(Mn_{0.7}Fe_{0.3})_{23}$ . (c) The plot of Kinetic energy (KE) of the Auger Fe  $L_3VV$  peak versus the incident  $h\nu$  relative to the Fe L-edge XAS maximum energy. The intersection point of the two dotted straight lines corresponds to the crossover energy of the resonant Raman to normal Auger regime. (d) The Co L-edge XAS and CIS spectra of  $Gd_6(Mn_{0.7}Co_{0.3})_{23}$ . (e) Co  $2p - 3d$  Res-PES difference spectra of  $Gd_6(Mn_{0.7}Co_{0.3})_{23}$ . (f) The plot of KE of the Co  $L_3VV$  Auger peak versus the incident  $h\nu$  relative to the Co L-edge XAS maximum energy. The intersection point of the two dotted straight lines corresponds to the crossover energy of the resonant Raman to normal Auger regime.

metal, which is surprising as it suggests that the Mn  $3d$  states in  $Gd_6Mn_{23}$  behave much like Mn metal.

### B. Two-hole correlations of $Gd_6(Mn_{0.7}Fe_{0.3})_{23}$ and $Gd_6(Mn_{0.7}Co_{0.3})_{23}$

Next, we carried out similar experiments for the Fe  $3d$  PDOS in  $Gd_6(Mn_{0.7}Fe_{0.3})_{23}$ . Figures 3(a)–3(c) show the Fe  $L$ -edge XAS and CIS, RES-PES difference spectra, and the plot of the BE of the Fe  $L_3VV$  Auger feature as a function of incident  $h\nu$  with respect to the XAS  $L_3$ -edge peak energy.

Figure 3(a) shows that the Fe  $L$ -edge XAS is also like Fe metal with single peak features for the  $L_3$  and  $L_2$  at photon energies of  $h\nu = 707.8$  eV and 720.5 eV, respectively. The spectra match well with Fe metal spectrum reported earlier [27]. The Fe  $2p$  soft x-ray PES with  $h\nu = 1000$  eV was also measured as shown in Supplemental Material [59] Fig. S1. It shows single peak Fe  $2p_{3/2}$  and  $2p_{1/2}$  features at a binding energy (BE) of 706.9 and 719.8 eV, and could be fitted with asymmetric Doniach-Sunjić line shapes, consistent with HAXPES results [58]. The peak positions and line shapes are consistent with Fe metal. The Fe  $L$ -edge CIS spectra of  $Gd_6(Mn_{0.7}Fe_{0.3})_{23}$  as

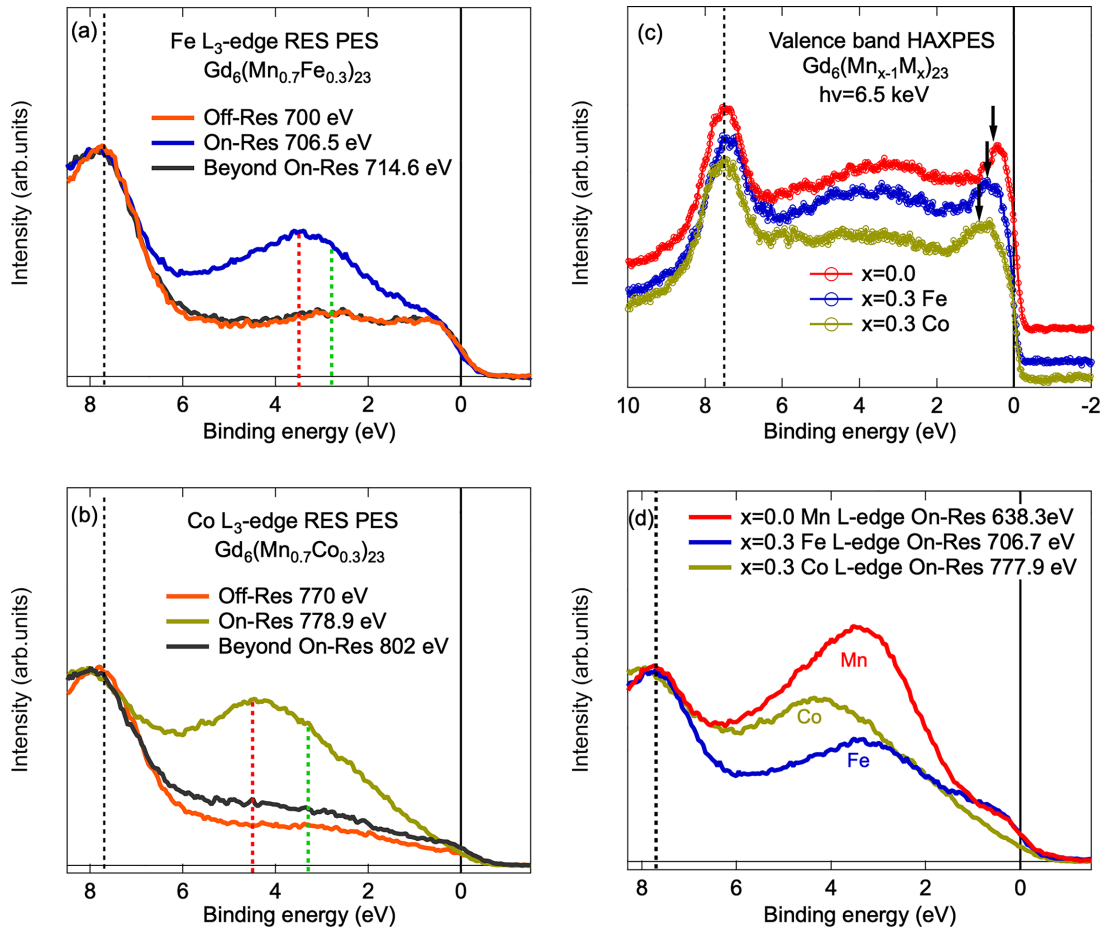


FIG. 4. (a) Selected Fe  $L_3$ -edge spectra for incident  $h\nu$  corresponding to off-resonance, on-resonance, and beyond on-resonance energy for  $\text{Gd}_6(\text{Mn}_{0.7}\text{Fe}_{0.3})_{23}$ . (b) Selected Co  $L_3$ -edge spectra for incident  $h\nu$  corresponding to off-resonance, on-resonance and beyond on-resonance energy for  $\text{Gd}_6(\text{Mn}_{0.7}\text{Co}_{0.3})_{23}$ . (c) HAXPES valence band spectra of  $\text{Gd}_6(\text{Mn})_{23}$ ,  $\text{Gd}_6(\text{Mn}_{0.7}\text{Fe}_{0.3})_{23}$ , and  $\text{Gd}_6(\text{Mn}_{0.7}\text{Co}_{0.3})_{23}$  measured with  $h\nu = 6.5$  keV. (d) Comparative  $L_3$ -edge on-resonance spectra for Mn, Fe, and Co in the resonant Raman region, just before it becomes a normal Auger feature.

investigated at BEs of 0.6 and 3.0 eV and they match with Fe  $L$ -edge XAS as shown in Fig. 3(a). The Fe  $L_3$ -edge RES-PES difference spectra of  $\text{Gd}_6(\text{Mn}_{0.7}\text{Fe}_{0.3})_{23}$  obtained from spectra measured at incident  $h\nu = 701.7\text{--}710.7$  eV (labeled A–G) are shown in Fig. 3(b). Here again, we observe a systematic increase of the two-hole correlation satellite at 4.4 eV BE for  $h\nu = 705.7$  and 706.7 eV (labeled B and C), and then from  $h\nu = 707.2\text{--}710.7$  eV (D–G), the satellite shifts to higher BEs from 4.0 to 7.5 eV BE. The Fe  $3d$  two-hole correlation satellite also exhibits a RRS to normal Auger transition as shown in Fig. 3(c).

Similarly, the corresponding experiments for the Co  $3d$  PDOS in  $\text{Gd}_6(\text{Mn}_{0.7}\text{Co}_{0.3})_{23}$  are shown in Figs. 3(d)–3(f). The Co  $L$ -edge XAS shows single peak features for the  $L_3$  and  $L_2$  at photon energies of  $h\nu = 778.0$  eV and 793.0 eV, respectively, consistent with Co metal [60]. The Co  $2p$  soft x-ray PES with  $h\nu = 1000$  eV (Fig. S1 of the Supplemental Material) shows single peak Co  $2p_{3/2}$  and  $2p_{1/2}$  features at a binding energy (BE) of 778.0 eV and 793.0 eV, and could be fitted with asymmetric Doniach-Sunjić line shapes, again consistent with Co metal [61]. The Co  $L$ -edge CIS spectra of  $\text{Gd}_6(\text{Mn}_{0.7}\text{Co}_{0.3})_{23}$  was investigated at BEs of 0.8 and 3.8 eV and they match with Co  $L$ -edge XAS as shown

in Fig. 3(d). The Co  $L_3$ -edge RES-PES difference spectra of  $\text{Gd}_6(\text{Mn}_{0.7}\text{Co}_{0.3})_{23}$  obtained from spectra measured with  $h\nu = 773.0\text{--}789.0$  eV (labeled A–I) are shown in Fig. 3(e). Here too, we see a systematic resonance of the two-hole correlation satellite, but at 4.4 eV BE for  $h\nu = 776.0$  and 777.9 eV (labeled B and C), and then from  $h\nu = 779.0\text{--}789.0$  eV (D to I), the satellite shifts to higher BEs from 5.5 to 15.5 eV BE. The Co  $3d$  two-hole correlation satellite also exhibits a RRS to normal Auger transition as shown in Fig. 3(f). The enhancement of the correlation satellite of Co  $3d$  PDOS is observed at a relatively higher BE of 4.4 eV compared to Mn and Fe  $3d$  PDOS, which showed correlation satellites at 3.3 and 3.6 eV BE. Hence, we measured the variation of the Co two-hole satellite over a larger  $h\nu$  range to clearly separate it from the Gd  $4f$  feature at 7.7 eV BE.

In Figs. 4(a) and 4(b), we plot selected spectra for incident  $h\nu$  corresponding to off-resonance, on-resonance (but in the resonant Raman region, i.e., just before it becomes a normal Auger feature and shifts in BE) and an energy far beyond resonance effects for  $\text{Gd}_6(\text{Mn}_{0.7}\text{Fe}_{0.3})_{23}$  and  $\text{Gd}_6(\text{Mn}_{0.7}\text{Co}_{0.3})_{23}$ . The spectra are normalized at the Gd  $4f$  peak (black dotted line). In  $\text{Gd}_6(\text{Mn}_{0.7}\text{Fe}_{0.3})_{23}$ , it is seen that the off-resonance and beyond resonance spectra shows Fe  $3d$  features just below

$E_F$  at a BE of 0.7 eV, and another broad feature at  $\sim 2.8$  eV (green dotted line), which is below the on-resonance maximum correlation satellite feature at 3.6 eV BE (red dotted line). Following the analysis of the Mn  $3d$  lower Hubbard band in Fig. 2, and the fact that the main Fe  $3d$  bands of Fe metal occur at less than 1 eV BE in SX-ARPES spectra reported for Fe metal [26], we associate the 0.7 eV feature with the coherent Fe  $3d$  band and the  $\sim 2.8$  eV feature with the lower Hubbard band of Fe. For  $\text{Gd}_6(\text{Mn}_{0.7}\text{Co}_{0.3})_{23}$ , while there is small feature just below  $E_F$  at about 0.5 to 1 eV BE, there is another weak broad asymmetric feature between 2.0 and 4.5 eV BE. We tentatively assign the shoulder of this broad feature associated with the off-resonance feature at  $\sim 3.3$  eV as the center of the weak lower Hubbard band (green dotted line), while the correlation satellite feature is at 4.4 eV BE (red dotted line). It is noted that the SX-ARPES of Co also showed that the main Co  $3d$  bands lie below 1 eV BE [26], and no clear signature of the lower Hubbard band in Co has been reported to date.

Alternatively, using the Cini-Sawatzky method [34–37], we can estimate the onsite Coulomb energy  $U_{dd}$  for the Mn  $3d$ , Fe  $3d$ , and Co  $3d$  states, from the  $L_3VV$  Auger features of our results. We use the equation which is valid in the Auger region, given by  $U_{dd(A)} = E_{2p} - (h\nu - E_{LVV}) - 2\epsilon_{3d}$  [27], where  $E_{2p}$  is the BE of the  $M 2p$  main peak,  $h\nu$  is the incident photon energy, and  $E_{LVV}$  corresponds to the BE of the Auger peak. In the equation,  $2\epsilon_{3d}$  represents the average two hole energy without correlations. We use the BE of the coherent feature in the off-resonant spectra discussed in Figs. 2, 3(a), and 3(b) as a suitable measure of  $\epsilon_{3d}$  because their Mn, Fe and Co  $3d$  character was confirmed by the CIS spectra, respectively. We also used the HAXPES valence band spectra of  $\text{Gd}_6(\text{Mn})_{23}$ ,  $\text{Gd}_6(\text{Mn}_{0.7}\text{Fe}_{0.3})_{23}$  and  $\text{Gd}_6(\text{Mn}_{0.7}\text{Co}_{0.3})_{23}$  to obtain an independent measure of  $\epsilon_{3d}$  [Fig. 4(c)]. The HAXPES spectra are normalized at the Gd  $4f$  peak (black dotted line). Since Gd  $5d$  cross-section is larger than Mn ( $5.5\times$ ), Fe ( $10\times$ ), and Co  $3d$  ( $2\times$ ) at a high energy of  $\sim 8$  keV, and smaller than Mn ( $7\times$ ), Fe ( $11\times$ ) and Co  $3d$  ( $6\times$ ) at a low energy of 600 eV [62], the relative spectral intensities between  $E_F$  and 6 eV BE are enhanced in HAXPES compared to soft x-ray results shown in Figs. 2–4. However, the changes seen in the HAXPES spectra are attributed to the TM  $3d$  states as the Gd  $5d$  states usually have a large bandwidth of  $\geq 5$  eV and a relatively small electron count ( $\leq 0.3$  electrons) in Gd intermetallics [63–65], as is also obtained in our electronic structure calculations discussed later. As seen in Fig. 4(c), the main  $3d$  band just below  $E_F$  is observed at 0.6 eV BE for  $x = 0.0$ , and it shows a slight shift to 0.7 eV for  $x = 0.3$  Fe and gets rounded with weaker intensity at 0.8 eV for  $x = 0.3$  Co. These values are close to the  $\epsilon_{3d} = 0.5, 0.6,$  and  $0.8$  eV from the off-resonant PES and the CIS spectra. Thus, the cross-sections indicate that the electronic states at  $E_F$  are dominated by the TM  $3d$  states.

Using the above described equation for  $U_{dd(A)}$ , and values of  $\epsilon_{3d}$ ,  $E_{2p}$  and  $E_{LVV}$  obtained from HAXPES and the  $L_3VV$  Auger spectral analyses for several  $h\nu$  values, we estimate the average onsite  $U_{dd} = 2.1 \pm 0.4$  eV for Mn,  $2.2 \text{ eV} \pm 0.4$  eV for Fe and  $2.9 \pm 0.4$  eV for Co. The detailed set of individual values for estimating the average onsite  $U_{dd}$  are listed

TABLE I. Comparison of magnetic moments (in  $\mu_B$ ) obtained with different values of  $U_{\text{Mn}}^{\text{DFT}}$  (in eV) and a fixed value of  $U_{\text{Gd}}^{\text{DFT}} = 6.5$  eV, except the case when  $U_{\text{Mn}}^{\text{DFT}} = U_{\text{Gd}}^{\text{DFT}} = 0.0$  eV. Values in square brackets are for Mn magnetic moments obtained from neutron diffraction (Ref. [42]).

$U_{\text{Mn}}^{\text{DFT}}$	0.0 eV	0.75 eV	1.5 eV	2.3 eV
Mn (4b) ( $\mu_B$ )	-2.27	-2.96[-2.8]	-3.27	-3.53
Mn (24d) ( $\mu_B$ )	-1.78	-2.57[-2.1]	-2.93	-3.30
Mn (32f <sub>1</sub> ) ( $\mu_B$ )	+1.64	+1.87[+1.8]	+3.12	+3.42
Mn (32f <sub>2</sub> ) ( $\mu_B$ )	+1.23	+1.76[+1.8]	+2.49	+2.83
net Mn/f.u. ( $\mu_B$ )	+9.89	+10.58	+24.64	+26.68
/Mn atom ( $\mu_B$ )	(+0.43)	(+0.46)	(+1.07)	(+1.16)
Gd/f.u. ( $\mu_B$ )	+42.12	+43.08	+43.14	+42.84
/Gd atom ( $\mu_B$ )	(+7.02)	(+7.18)	(+7.19)	(+7.14)
$M_{\text{Tot}}$ ( $\mu_B$ )	52.01	53.66	67.78	69.52

$M_{\text{Tot}} = 54.7 \mu_B$  from bulk magnetization for an applied field  $H = 5\text{T}$  (ref. 47). f.u.: formula unit.

with error bars in Table I of the Supplemental Material. It is also noted that the Gd  $4f$  states are observed at a BE of  $7.6 \pm 0.3$  eV for all the three cases of  $x = 0.0, 0.3$  Fe, and  $0.3$  Co. As mentioned in the introduction, from a combination of valence band PES and conduction band I-PES,  $U_{ff} \sim 11$  eV for Gd metal [21]. As seen in the HAXPES valence band spectra, the Gd  $4f$  states are observed at the same BE in our results as in Gd metal, indicating  $U_{ff} \sim 11$  eV for  $x = 0.0, 0.3$  Fe, and  $0.3$  Co. In Fig. 4(d), we compare the on-resonance spectra in the resonant Raman region for  $x = 0.0, 0.3$  Fe, and  $0.3$  Co with the spectra normalized at the Gd  $4f$  peak (black dotted line). It is clearly seen that the spectral intensity of the Fe PDOS at and near  $E_F$  of the  $x = 0.3$  Fe case is quite close to that of the Mn  $3d$  PDOS of  $x = 0.0$  parent, while the Co PDOS at and near  $E_F$  of the  $x = 0.3$  Co case is significantly suppressed compared to the Mn  $3d$  PDOS of  $x = 0.0$  parent. Further, as shown in Supplemental Material Fig. S2, the Mn  $3d$  PDOS of  $x = 0.3$  Fe and  $0.3$  Co also shows the same behavior. Based on known theoretical results of DMFT calculations of the one-band Hubbard model [66] as a function of  $U/W$ , the observed spectral differences indicate that the TM  $3d$  states in  $\text{Gd}_6(\text{Mn}_{0.7}\text{Co}_{0.3})_{23}$  exhibit a larger  $U/W$  and are more strongly correlated compared to  $\text{Gd}_6(\text{Mn}_{0.7}\text{Fe}_{0.3})_{23}$   $3d$  states.

To understand the relation of the  $U_{dd(A)}$  estimated from experiment with the Hubbard onsite Coulomb energy  $U_{dd(H)}$  between two  $d$  electrons (which corresponds to the ‘process’  $2M \rightarrow M^- + M^+$ ), we calculated the energies of the photoemission and two hole Auger final states for the  $d^n$  configuration. The photoemission final state spectrum corresponds to the process  $d^n \rightarrow d^{n-1}$  while the Auger final state spectrum corresponds to the process  $d^n \rightarrow d^{n-2}$ . The photoemission and Auger spectra can be obtained easily in the limit of very small bandwidth  $W$  with respect to the Hubbard energy ( $W \ll U_{dd(H)}$ ). In this limit, the electronic configuration is a pure  $d^n$  configuration with energy per atom:

$$E(d^n) = n\epsilon_d + \frac{n(n-1)}{2}U_{dd(H)},$$



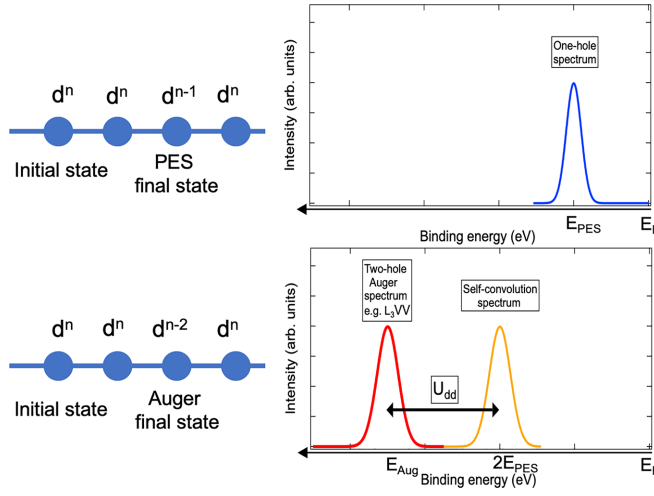


FIG. 5. Left: Final states of the photoemission ( $d^{n-1}$ ) and Auger ( $d^{n-2}$ ) process for the  $d^n$  initial state. Right: Schematic photoemission and Auger spectra. The blue spectrum is the photoemission (one-hole) feature at energy  $E_{\text{PES}} = E(d^{n-1}) - E(d^n)$ . The dark yellow spectrum centered at energy  $2E_{\text{PES}}$  shows the self-convoluted PES feature and corresponds to two independent holes in the valence band. The red spectrum is the Auger spectrum with two onsite holes in the final state at an energy  $E_{\text{Aug}} = E(d^{n-2}) - E(d^n)$ .

where  $\varepsilon_d$  is the one-electron energy of a  $d$  state. In the photoemission process, one  $d$  electron is removed and the transition energy is given by

$$E_{\text{PES}} = E(d^{n-1}) - E(d^n) = -\varepsilon_d - (n-1)U_{dd(H)},$$

and a peak is expected at  $E_{\text{PES}}$  in the photoemission spectrum (see Fig. 5). The self-convolution of the photoemission spectrum shows a peak at an energy  $2E_{\text{PES}}$  and represents two independent holes in the valence band. In the Auger process, the final state configuration of the photoexcited site is  $d^{n-2}$  and the Auger peak energy is given by

$$E_{\text{Aug}} = E(d^{n-2}) - E(d^n) = -2\varepsilon_d - (2n-3)U_{dd(H)},$$

$$U_{dd(A)} = E_{\text{Aug}} - 2E_{\text{PES}}$$

$$= -2\varepsilon_d - (2n-3)U_{dd(H)} - 2[-\varepsilon_d - (n-1)U_{dd(H)}]$$

$$= U_{dd(H)}.$$

A schematic picture describing this equivalence in the small bandwidth limit is shown in Fig. 5. To check this equivalence, it is important to compare the theoretically estimated  $U_{dd(H)}$  values reported in the literature with the  $U_{dd(A)}$  values obtained from the present experiments. If we consider, for example, the metal LVV Auger spectrum, it corresponds to an initial core hole in the L-edge and VV corresponds to two valence band holes in the final state. Then the energy of the two-holes on the same site in the Auger final state,  $U_{dd(A)}$ , compared to the self-convolution of the one hole photoemission spectrum, provides a measure of the onsite Coulomb energy (Fig. 5).

Using first principles LDA+DMFT calculations for a realistic five-band model and comparing with ARPES results, Biermann *et al.* [25] showed that  $U_{dd(H)} = 3.0$  eV for Mn metal, while we obtain a value of  $U_{dd(A)} = 2.1 \pm 0.4$  eV for

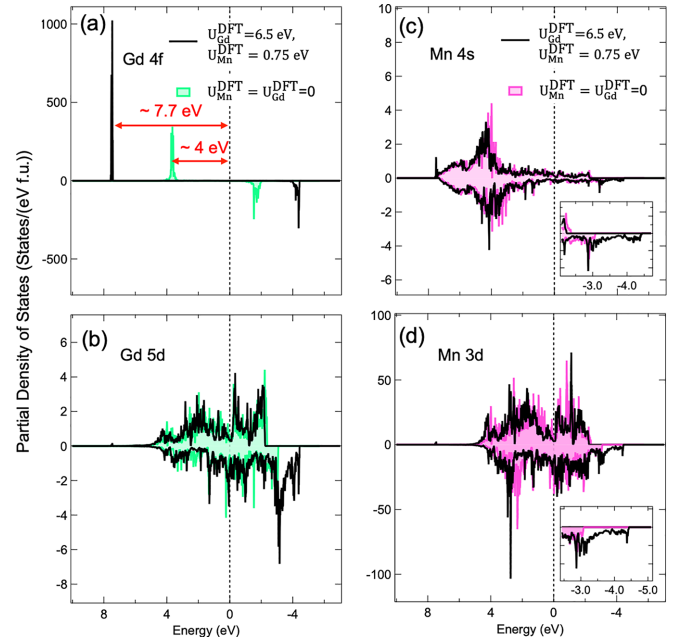


FIG. 6. The calculated PDOS of (a) Gd  $4f$ , (b) Gd  $5d$ , (c) Mn  $4s$ , and (d) Mn  $3d$  for  $\text{Gd}_6\text{Mn}_{23}$ , showing the majority and minority spin states obtained from electronic structure calculations of  $\text{Gd}_6\text{Mn}_{23}$ . In each panel, the colored curves show the PDOS for  $U_{\text{Mn}}^{\text{DFT}} = 0.0$  and  $U_{\text{Gd}}^{\text{DFT}} = 0.0$ , while the black curves show the PDOS for  $U_{\text{Mn}}^{\text{DFT}} = 0.75$  eV and  $U_{\text{Gd}}^{\text{DFT}} = 6.5$  eV. In panel (a), the Gd  $4f$  states for  $U_{\text{Mn}}^{\text{DFT}} = 0.0$  and  $U_{\text{Gd}}^{\text{DFT}} = 0.0$  are seen at  $\sim 4$  eV BE below  $E_F$ , while for  $U_{\text{Mn}}^{\text{DFT}} = 0.75$  eV and  $U_{\text{Gd}}^{\text{DFT}} = 6.5$  eV, the Gd  $4f$  states are seen at  $\sim 7.7$  eV BE below  $E_F$ . The insets in panels (c) and (d) show the corresponding differences on an expanded scale for Mn  $4s$ , and Mn  $3d$  PDOS, respectively. Note the different y scales for all panels.

Mn in  $\text{Gd}_6\text{Mn}_{23}$ . However, using LSDA+DMFT calculations for Fe and Co metal and comparing with spin-resolved ARPES results, Sanchez-Barriga *et al.* [26] showed that  $U_{dd(H)} = 1.5$  eV for Fe metal, and 2.5 eV for Co metal, while we obtain  $U_{dd(A)} = 2.2 \pm 0.4$  eV for Fe in  $\text{Gd}_6(\text{Mn}_{0.7}\text{Fe}_{0.3})_{23}$ , and  $U_{dd(A)} = 2.9 \pm 0.4$  eV for Co in  $\text{Gd}_6(\text{Mn}_{0.7}\text{Co}_{0.3})_{23}$ . The results indicate that  $U_{dd(A)}$  in intermetallics are fairly close to the  $U_{dd(H)}$  values estimated for elemental metals.

In Figs. 6(a)–6(d), we show the DFT+ $U$  spin-polarized generalized-gradient approximation (GGA) electronic structure calculations for  $\text{Gd}_6\text{Mn}_{23}$ . Each panel shows the calculations without onsite Coulomb energies, i.e.,  $U_{\text{Mn}}^{\text{DFT}} = 0.0$  and  $U_{\text{Gd}}^{\text{DFT}} = 0.0$  (colored curves), compared with calculations with onsite Coulomb energies  $U_{\text{Mn}}^{\text{DFT}} = 0.75$  eV and  $U_{\text{Gd}}^{\text{DFT}} = 6.5$  eV. It can be seen in Fig. 6(a) that when  $U_{\text{Mn}}^{\text{DFT}} = 0.0$  and  $U_{\text{Gd}}^{\text{DFT}} = 0.0$ , the Gd  $4f$  states occur as a sharp feature at about 4 eV BE in the occupied states below  $E_F$  and nearly 2 eV above  $E_F$ . However, with  $U_{\text{Mn}}^{\text{DFT}} = 0.75$  eV and  $U_{\text{Gd}}^{\text{DFT}} = 6.5$  eV, the Gd  $4f$  states occur as a sharp feature at about 7.7 eV BE in the occupied states and about 4.5 eV above  $E_F$ . For these values of  $U_{\text{Mn}}^{\text{DFT}}$  and  $U_{\text{Gd}}^{\text{DFT}}$ , we obtain the Gd and Mn magnetic moments in agreement with reported bulk magnetization [47], neutron diffraction [42] results. Table I shows the Mn magnetic moments obtained for different values of  $U_{\text{Mn}}^{\text{DFT}}$  varied from 0.0 to 2.3 eV, and the magnetic moments

from neutron diffraction (values in Table I square brackets) are consistent with those obtained for  $U_{\text{Mn}}^{\text{DFT}} = 0.75$  eV. Here,  $U_{\text{Mn}}^{\text{DFT}} = U_{\text{Mn}}^{\text{eff}} = U_{dd} - J_{dd}$  and assuming  $J_{dd} = 0.9$  eV based on earlier work [67], the results imply that  $U_{dd} = 1.65$  eV and is fairly close to the estimated  $U_{dd(A)} = 2.1 \pm 0.4$  eV obtained from the Cini-Sawatzky method. As seen in Figs. 6(b) and 6(c), the Gd  $5d$  and Mn  $4s$  PDOS are relatively very weak compared to the Gd  $4f$  states. The Gd  $5d$  states plotted in Fig. 6(b) are spread from 5 eV BE below  $E_F$  to nearly 3 eV above  $E_F$  without  $U^{\text{DFT}}$ , but the minority states get shifted compared to the majority states with  $U^{\text{DFT}}$ . However, in Fig. 6(c), while the Mn  $4s$  states are spread over a larger range from nearly 8 eV BE below  $E_F$  to nearly 3 eV above  $E_F$  without  $U^{\text{DFT}}$ , they also show a similar shift on including  $U^{\text{DFT}}$  [inset of Fig. 6(c)].

The Mn  $3d$  PDOS show roughly  $\sim 10$  times higher weight compared to Gd  $5d$  and Mn  $4s$  PDOS, and are spread from 5 eV BE below  $E_F$  to nearly 3 eV above  $E_F$  when  $U^{\text{DFT}} = 0$  [Fig. 6(d)], but they show a clear shift of the minority states compared to the majority states on including  $U^{\text{DFT}}$  [inset of Fig. 6(d)]. This leads to an increase in magnetic moments and gives values consistent with experiment.  $U_{\text{Mn}}^{\text{DFT}}$  was varied from 0.0 to 2.3 eV to obtain optimal magnetic moments as listed in Table I. The magnetic moment values obtained for  $U_{\text{Mn}}^{\text{DFT}} = 0.75$  eV are quite close to the experimental values, while for  $U_{\text{Mn}}^{\text{DFT}} = 0.0$  eV, the magnetic moments are smaller and for  $U_{\text{Mn}}^{\text{DFT}} = 1.5$  and 2.3 eV, they are larger than the experimental values. It is noted that the Cini-Sawatzky method gives us a single broad Auger feature and consequently, a single value of  $U_{dd(A)}$  for Mn with an error bar of  $\pm 0.4$  eV, although there are four types of Mn sites in  $\text{Gd}_6\text{Mn}_{23}$ . While the Mn magnetic moments can be clubbed into two types of Mn sites, two sites with up-spins and two sites with down-spins, nonetheless, it must be remembered that the Cini-Sawatzky method gives us an approximate value for the  $U_{dd(A)}$  for all Mn sites. However, the electronic structure results are considered reliable because we get four different values of Mn magnetic moments for the four Mn sites, fairly consistent with values obtained from neutron diffraction (see Table I, values in square brackets) [42].

For the case of Gd magnetic moments, it is well-known that Gd  $4f$  states behave like strongly localized  $\text{Gd}^{3+} 4f^7$  configuration with  $S = 7/2$  in elemental Gd metal as well as in Gd alloys [63–65]. Early work on Gd metal showed that its ground state can be described by a single Slater determinant and a one electron DFT is valid [68,69]. It was shown that the average energies of the onsite Coulomb  $U_{ff}$  and exchange  $J_{ff}$  interaction could be calculated using the local spin-density approximation [68,69]. By comparing with the experimental  $N-1$  and  $N+1$  final states from photoemission and inverse-photoemission spectra of Gd metal [21], it was shown that  $U_{ff} = 6.7$  eV and  $J_{ff} = 0.7$  eV, and  $U_{\text{Gd}}^{\text{eff}} = U_{ff} + 6J_{ff} \approx 11$  eV. Based on the Dudarev approach [53],  $U_{\text{Gd}}^{\text{DFT}} = U_{ff} - J_{ff}$  was varied from 6.0 to 12 eV to obtain PDOS consistent with experiment. Using the obtained PDOS, we simulated the calculated valence band spectrum to compare with the experimental valence band spectrum [62]. The calculated spectrum was obtained by multiplying the PDOS with known photoionization cross-sections at 1000 eV [62] and convoluted with a Gaussian function (1.0 eV FWHM for

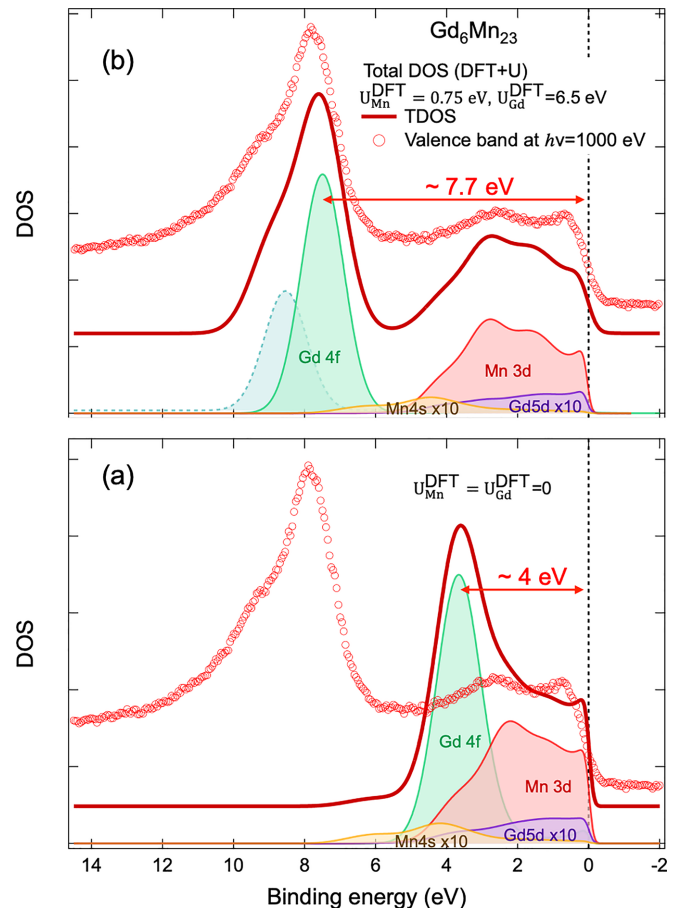


FIG. 7. Comparison of the calculated spectrum of  $\text{Gd}_6\text{Mn}_{23}$  with the experimental spectrum of  $\text{Gd}_6\text{Mn}_{23}$ . Panel (a) shows the spectrum simulated using PDOS obtained with  $U_{\text{Mn}}^{\text{DFT}} = 0.0$  and  $U_{\text{Gd}}^{\text{DFT}} = 0.0$ . Panel (b) shows the spectrum simulated using PDOS obtained with  $U_{\text{Mn}}^{\text{DFT}} = 0.75$  eV and  $U_{\text{Gd}}^{\text{DFT}} = 6.5$  eV. The Gd  $4f$  and Mn  $3d$  occupied partial DOS show features consistent with the experimental spectrum. The weak shoulder at  $\sim 8.8$  eV BE is attributed to the surface Gd  $4f$  states and is simulated as a replica of the main Gd  $4f$  feature with reduced intensity. For soft x-ray PES, the Mn  $4s$  and Gd  $5d$  cross-sections are very weak and lead to very small intensities in the spectrum.

Mn  $3d$ , Mn  $3s$ , and Gd  $5d$  PDOS; and 1.5 eV FWHM for Gd  $4f$  PDOS). The results are shown in Fig. 7(a) for the case without onsite Coulomb energies, while Fig. 7(b) shows the calculations with onsite Coulomb energies and Hund's coupling.

It is clear that the calculated spectrum without onsite Coulomb energies does not match with the experimental spectrum, as shown in Fig. 7(a). However, based on the comparison shown in Fig. 7(b) of the calculated spectrum with onsite Coulomb energies and Hund's coupling, we find that  $U_{\text{Gd}}^{\text{DFT}} = 6.5$  eV gives a fair match with experiment. The comparison of soft x-ray PES [Fig. 7(b), same as in Fig. 2(e)] and HAXPES [Fig. 4(c)] valence band spectra allows us to identify the weak feature at about 8.8 eV BE in the soft x-ray PES spectrum to be due to Gd  $4f$  surface states, as this feature is missing in bulk sensitive HAXPES spectrum. Further, the average magnetic moment of Gd is calculated

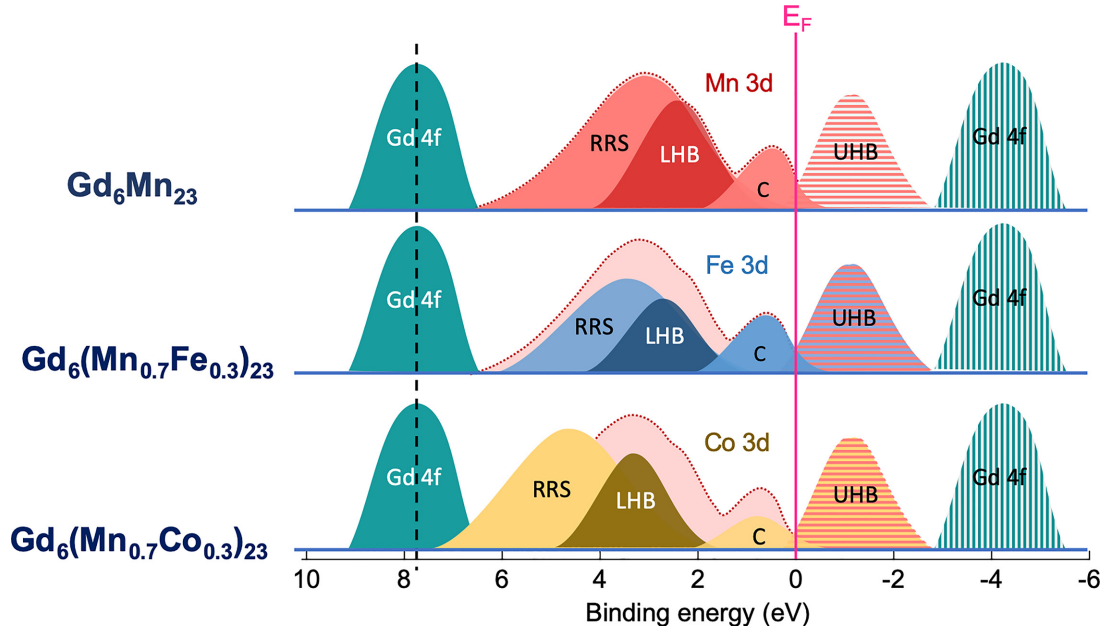


FIG. 8. Schematic of the occupied and unoccupied electronic structure of  $\text{Gd}_6\text{Mn}_{23}$ ,  $\text{Gd}_6(\text{Mn}_{0.7}\text{Fe}_{0.3})_{23}$ , and  $\text{Gd}_6(\text{Mn}_{0.7}\text{Co}_{0.3})_{23}$ , showing the Mn, Fe, and Co Lower and Upper Hubbard bands (LHB, UHB), the coherent feature (C), the resonant Raman satellite (RRS) feature, and the Gd 4f occupied and unoccupied states.

to be  $\mu_{\text{Gd}} = +7.18 \mu_B$ , in good agreement with the localized  $\text{Gd}^{3+} 4f^7$  configuration. Assuming  $J_{ff} = 0.7$  eV as is known for Gd metal [68,69], we obtain for  $\text{Gd}_6\text{Mn}_{23}$ ,  $U_{\text{Gd}}^{\text{eff}} = U_{ff} + 6J_{ff} = U_{\text{Gd}}^{\text{DFT}} + 7J_{ff} = 11.4$  eV. This value is close to the  $U_{\text{Gd}}^{\text{eff}} \approx 11$  eV of Gd metal [21], and is expected for the localized Gd 4f states in  $\text{Gd}_6\text{Mn}_{23}$ .

In Fig. 8, we have plotted the schematic electronic structure of  $\text{Gd}_6\text{Mn}_{23}$  and how it gets modified by Fe and Co substitution. In particular, we identify the Mn 3d occupied and unoccupied states lying between the localized  $\text{Gd}^{3+}$  occupied and unoccupied states. Further, the Mn 3d states split into coherent states at and near  $E_F$  and the lower Hubbard band (LHB) of  $\text{Gd}_6\text{Mn}_{23}$  is at 2.7 eV BE. Upon Fe substitution, the Fe 3d states lie very close to Mn 3d states and essentially exhibit very similar coherent states as well as a lower Hubbard band at slightly higher BE. Moreover, the relative spectral intensities of the coherent states and LHBs in  $\text{Gd}_6(\text{Mn}_{0.7}\text{Fe}_{0.3})_{23}$  are also very similar [Fig. 4(a)], suggesting a similar  $U_{dd}/W$ , the ratio of onsite Coulomb energy to the coherent band width  $W$ . This is borne out by the fact that the Mn and Fe 3d states show very similar values of  $U_{dd(A)} = 2.1 \pm 0.4$  eV and  $2.2 \pm 0.4$  eV. In contrast, with Co substitution, the position of the LHB is at a higher BE and the relative intensity of the Co 3d coherent states is lower in  $\text{Gd}_6(\text{Mn}_{0.7}\text{Co}_{0.3})_{23}$  [Fig. 4(b)], suggesting stronger correlations which is consistent with the relatively larger  $U_{dd(A)} = 2.9 \pm 0.4$  eV for Co.

Thus, the lower relative intensity of the 3d states at  $E_F$  indicate that the effective carrier density is reduced in  $\text{Gd}_6(\text{Mn}_{0.7}\text{Co}_{0.3})_{23}$  compared to  $\text{Gd}_6(\text{Mn}_{0.7}\text{Fe}_{0.3})_{23}$ . This is expected to reduce the specific-heat Sommerfeld coefficient  $\gamma$  in  $\text{Gd}_6(\text{Mn}_{0.7}\text{Co}_{0.3})_{23}$  and alter the conductivity significantly compared to  $\text{Gd}_6(\text{Mn}_{0.7}\text{Fe}_{0.3})_{23}$ . The overall results indicate that the TM onsite Coulomb correlations are mainly responsible for the electronic transport properties derived from the

carriers at  $E_F$ , while the more strongly correlated  $f$  electron states are situated far from  $E_F$ .

#### IV. CONCLUSIONS

In conclusion, the electronic structure and 3d partial density of states of the ferrimagnetic materials  $\text{Gd}_6(\text{Mn}_{1-x}\text{M}_x)_{23}$  ( $M = \text{Fe}, \text{Co}; x = 0.0, 0.3$ ) was investigated using x-ray absorption, soft x-ray, hard-x-ray, resonant photoemission, and constant initial state spectroscopy. We could estimate an average  $U_{dd} = 2.1 \pm 0.4$  eV,  $2.2 \pm 0.4$  eV, and  $2.9 \pm 0.4$  eV for the Mn 3d, Fe 3d, and Co 3d states, respectively. The relatively larger  $U_{dd}$  for Co compared to Fe 3d states results in lower DOS for the coherent feature at  $E_F$  and higher DOS in the lower Hubbard band away from  $E_F$  in  $\text{Gd}_6(\text{Mn}_{0.7}\text{Co}_{0.3})_{23}$  compared to  $\text{Gd}_6(\text{Mn}_{0.7}\text{Fe}_{0.3})_{23}$ . The DFT+ $U$  electronic structure calculations for the parent  $\text{Gd}_6\text{Mn}_{23}$  showed that the calculated Mn magnetic moments are consistent with experiments for  $U_{dd} = 1.65$  eV and  $J_{dd} = 0.9$  eV. We could also simulate the  $\text{Gd}_6\text{Mn}_{23}$  valence band spectrum to be fairly consistent with the experimentally measured spectrum for  $U_{\text{Gd}}^{\text{DFT}} = 6.5$  eV and  $J_{ff} = 0.7$  eV. The results indicate the crucial role of  $d$ - $d$  correlations in the presence of large  $f$ - $f$  correlations for tuning the electronic structure and magnetic properties of RE-TM intermetallics.

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