Estimate of the Coulomb correlation energy in CeAg₂Ge₂ from inverse photoemission and high resolution photoemission spectroscopy

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Abstract
The occupied and the unoccupied electronic structure of CeAg₂Ge₂ single crystal has been studied using high resolution photoemission and inverse photoemission spectroscopy, respectively. High resolution photoemission reveals the clear signature of Ce 4f states in the occupied electronic structure which was not observed clearly in our earlier studies. The Coulomb correlation energy in this system has been determined experimentally from the position of the 4f states above and below the Fermi level. Theoretically, the correlation energy has been determined by using the first principles density functional calculations within the generalized gradient approximations taking into account the strong intra-atomic (on-site) interaction Hubbard Ueff term. The calculated valence band shows minor changes in the spectral shape with increasing Ueff due to the fact that the density of Ce 4f state is narrow in the occupied part and is hybridized with the Ce 5d, Ag 4d and Ge 4p states. On the other hand, substantial changes are observed in the spectral shape of the calculated conduction band with increasing Ueff since the density of Ce 4f state is very large in the unoccupied part, compared to other states. The estimated value of correlation energy for CeAg₂Ge₂ from the experiment and the theory is ≈ 4.2 eV. The resonant photoemission data are analyzed in the framework of the single-impurity Anderson model which further confirms the presence of the Coulomb correlation energy and small hybridization in this system.

Keywords: photoemission and photoelectron spectra, electron density of states, strongly correlated electron systems

(Some figures may appear in colour only in the online journal)
1. Introduction

Ce-based systems show various ground states like magnetic, non-magnetic and superconducting phases [1–4]. The unusual properties in these systems mainly depends on two important factors: (1) the strong Coulomb interaction within the 4f shell and (2) the hybridization between the partially delocalized 4f electrons and the non-4f-band electrons [5–7]. It is well known that the 4f electron in Ce lies at the boundary between itinerant and localized character giving rise to two different phases α and γ which are isosstructural but with distinctly different electronic structures. The γ phase is a metal with a local moment formed by the localization of the 4f electron and hence responsible for paramagnetism in these γ-Ce-based systems. The hybridization between the delocalized 4f states with the other states is reported to be less in the γ phase [1, 8]. On the other hand, the α phase has delocalized 4f electrons which are more or less of itinerant character that give rise to non-magnetic behavior. The α phase is known to be the Fermi liquid phase where the effective mass of the 5d state is enhanced due to high hybridization with the 4f electrons. Theoretical calculation shows that the 4f bands are broader for the α phase than the γ phase, although the occupation of the occupied part below the Fermi level stays more or less the same [9]. However, the photoemission (PES) spectra for the Ce-based system shows that the 4f states are more localized away from the Fermi level ($E_F$) and have an itinerant character near $E_F$. On comparing the PES spectra with the band structure calculation, the difference arises mainly for the γ phase where a large density of localized 4f states appears at the higher energy in the experiment but theory doesn’t show such a large density of localized 4f states. It is well known that the localized 4f states are related to the electron–electron Coulomb correlation present in these Ce-based systems and hence it is important to determine it from both experiment and theory.

In the present work, we have revisited the electronic structure of CeAg$_2$Ge$_2$ which has a γ-Ce phase to understand the localized and itinerant character of Ce 4f states in this system and also to determine the Coulomb correlation energy experimentally. The electronic structure of CeAg$_2$Ge$_2$ was studied by us earlier in detail by resonant photoemission (RPES) and angle resolved photoemission spectroscopy (ARPES) [10, 11]. CeAg$_2$Ge$_2$ is paramagnetic at room temperature and shows the anisotropic magnetic properties with antiferromagnetic transition at 4.6 K [12]. Ce is found to be in the trivalent state in CeAg$_2$Ge$_2$ from the x-ray photoemission measurement. The hybridization strength = 0.19 eV in this system has been determined from Ce 3d core level analysis [10]. RPES showed two resonance features in the valence band spectra related to Ce 4f states of localized and itinerant character [10]. We have found that the occupied electronic structure of CeAg$_2$Ge$_2$ and the character of the Ce 4f states both localized and itinerant could very well be explained from the theoretical calculation without considering the electron–electron correlation term [10, 11]. However the presence of correlation in these Ce-based systems affects the spectral shape of the valence band PES spectra [13] and there is a need to carry such experiments with very high resolution [14]. The earlier PES measurements were performed with 400 meV experimental resolution, and so from the valence band spectral shape the correlation energy in this system could not be estimated. Hence, in the present work the valence band of CeAg$_2$Ge$_2$ is probed with higher experimental resolution (20 meV). Also for the Ce metal the effect of correlation has been reported to be more evident in the unoccupied part of the electronic structure than the occupied part [15, 16]. Hence, it is of interest to study the unoccupied part of the electronic structure of CeAg$_2$Ge$_2$ by inverse photoemission spectroscopy (IPES). Therefore, in the present work, we have determined the electron correlation energy ($U$) for CeAg$_2$Ge$_2$ experimentally from the PES and IPES spectra. Theoretically, there are two approaches to understand the character of the Ce 4f electrons: (1) band structure calculation and (2) model Hamiltonian-based calculation. Using the band structure calculation with GGA + U the correlation energy $U_{\text{eff}}$ has been determined and compared with the experimental $U$. Using the second approach a single-impurity Anderson model (SIAM) is used to understand the correlation and hybridization in this system. In the SIAM picture the Ce atoms in the CeAg$_2$Ge$_2$ system are considered to be a set of independent impurities and it has been proven to be quite successful in interpreting the RPES data.

2. Methods

CeAg$_2$Ge$_2$ single crystal was grown by the self-flux method [12]. High resolution photoemission measurements at 20 meV resolution were performed at the high-resolution photoelectron spectroscopy station of TEMPO beamline at Synchrotron SOLEIL, France [17] and also at APE beamline of Synchrotron Elettra, Italy [18]. The clean surface of the CeAg$_2$Ge$_2$ single crystal was obtained by cleaving the sample in-situ in a base pressure of 9 × 10$^{-11}$ mbar and at a temperature of about 40 K. The data were recorded with a Scienta SES 2002 electron energy analyzer. The photoemission measurements with 400 meV resolution were carried out at the angle-integrated PES beamline on the Indus-1 synchrotron radiation source, India [19]. The binding energy in the photoemission spectra has been determined with reference to the Fermi level of the clean Gold surface that is in electrical contact with the sample at the same experimental conditions [10]. IPES experiments were performed under ultrahigh vacuum at a base pressure of 2 \times 10^{-10} mbar in a separate chamber. To obtain an atomically clean surface the sample was sputtered with 1.5 keV argon ions and annealed at 500 K [10]. An electrostatically focused electron gun of Stoffel Johnson design and an acetone gas filled photon detector with a CaF$_2$ window was used for the IPES experiments [20]. IPES was performed in the isochromat mode where the kinetic energy of the incident electrons has been varied at 0.05 eV steps and photons of fixed energy (9.9 eV) are detected with an overall resolution of 0.55 eV [20]. Similar to the PES measurement, in IPES also the binding energy was determined with reference to the Fermi level of the clean Silver surface that is in electrical contact with the sample at the same experimental conditions. In
both the PES and IPES experiments, the incident angle and the take off angle were kept fixed at 45 degrees. The RPES spectrum was analysed in the framework of SIAM which uses the variational approach of Gunnarsson and Schönhammer. The details of the SIAM numerical procedure is reported in the reference [21].

The spin-polarized electronic structure calculations were performed using the density-functional theory (DFT) [22] and a very accurate full-potential linear augmented plane-wave (FP-LAPW) approach incorporating the spin-orbit (SO) coupling as implemented in WIEN2K code [23]. This is an implementation of a FP-LAPW plus local orbitals (LAPW + lo) method [24] within the DFT. The Perdew, Burke, Ernzerhof (PBE) [25] gradient corrected local spin density approximation (LSDA-GGA) for the exchange correlation (XC) potential was used. The spin-orbit (SO) interaction was treated by the second-variational approach [24, 26]. A plane wave expansion with \( R_{MT} \times K_{\text{max}} \) equal to 8 and the dependence of the total energy on the number of \( k \) points in the irreducible edge of the first Brillouin zone was explored within the linearized tetrahedron scheme by performing the calculation for 405 \( k \) points (17 \( \times \) 17 \( \times \) 17 mesh). The cut-off for charge density was fixed at \( G_{\text{max}} = 14 \). The muffin-tin radii used for the calculations were 2.9, 2.4 and 2.1 Bohrs for Ce, Ag and Ge, respectively. To account for the Coulomb correlation interaction within the Ce-4f shell, we additionally considered the PBE XC potential corrected according to the GGA + U method [27, 28]. For Ce, the values of \( U_{\text{eff}} = U - J \) with \( J = 0.95 \) eV were varied in turn by taking it to be 1.4 eV, 2.7 eV, 3.4 eV, 4 eV, 4.2 eV and 5.4 eV respectively. In the calculation \( U \) and \( J \) do not enter separately; hence the difference \( U_{\text{eff}} = U - J \) is meaningful [29] and has been compared with the experimental \( U \). To determine the ground state of the system, we adopted a standard procedure of minimizing the total energy as a function of lattice parameters \((a, c/a)\). We also performed the atomic position optimization such that the residual force on each atom was less than 1 meV Å\(^{-1}\). The equilibrium lattice parameter \( a \) was calculated to be 4.313 Å with \( c/a = 2.572 \) which agrees well with the experimental value of \( a = 4.301 \) Å (and \( c/a = 2.551 \) [12]). The relaxed ionic positions for Ce: (0,0,0); Ag: (0.0,5.0,25); and Ge: (0.0,0,391) closely match experimental values of Ce: (0,0,0); Ag: (0,0,5,0,25); and Ge:(0,0,0,389) [12].

### 3. Results and discussions

Basically, the electron correlation energy \( U \) is the energy required to transfer an electron within the same band between two ions in a solid which are initially in the same valence state [30, 31]. For Ce metal and its compounds in the trivalent state, \( U \) is the energy to produce an Ce\(^{2+}\) and an Ce\(^{4+}\) ion by transferring an electron from one Ce\(^{3+}\) ion to another. Hence, \( U \) can be derived experimentally from the position of the 4f states above and below \( E_F \) from the valence and conduction band using PES and IPES respectively [15, 32–34].

In figure 1, we have shown the influence of the resolution on the PES spectra for the experiments carried out at two different energy resolutions of 20 meV and 400 meV. Generally, for Ce metal and its compounds the peak structure pinned at \( E_F \) corresponds to \( f^{5/2} \) final state, whereas the peak at 280 meV corresponds to \( f^{15/2} \) final state [14]. The intensity ratio of \( f^{5/2}f^{15/2} \) is related to the hybridization strength as shown for Ce 4f states in CeN\(_3\)Al\(_3\) and CeNiAl\(_3\) [35]. In Ce alloys, \( f^{17/2} \) and \( f^{3/2} \) features can appear due to magnetic Ce 4f states as well as due to the Kondo singlets formed via quantum entanglement of the 4f states with the conduction electron states [13, 14]. The appearance of \( f^{13/2} \) and \( f^{3/2} \) features in CeAg\(_2\)Ge\(_2\) is mainly due to the magnetic nature of Ce in this system [12]. Figure 1 shows a clear difference in the two spectra for the \( f^{3/2} \) excitation (marked by tick near \( E_F \) in figure 1) which is more prominent in the high resolution 20 meV spectra. Hence, the value of spin orbit splitting can be obtained from the high resolution spectra, as shown in the inset of figure 1. The spin orbit splitting \( \Delta \) between \( f^{17/2} \) and \( f^{3/2} \) is found to be 280 meV which is in good agreement with the other Ce-based systems [14]. The 4f\(^{12} \) feature of Ce marked by the tick in figure 1 is located at \(-1.7 \) eV and is very broad for both the spectra recorded with 20 meV and 400 meV resolution. In the inset of figure 1, we have compared the on-resonance spectra at \( h\nu = 121 \) eV with the off-resonance spectra at \( h\nu = 80 \) eV for the PES measurement carried out at high resolution. There is a negligible signature of the Ce 4f\(^{12} \) feature in the off-resonance spectra. This clearly signifies the importance of RPES, to identify the position of the Ce 4f features in the valence band. The shapes of the \( f^{3/2} \) and \( f^{15/2} \) features indicates that Ce in this system is \( \gamma \)-type [14]. The \( f^{13/2} \) excitation in the spectra with 400 meV resolution is not clearly distinguishable because the resolution is more than the spin orbit splitting. The effect of the instrumental resolution in determining the Ce 4f features has also been shown for CeAl\(_2\) alloy [14, 36, 37]. Hence, figure 1 clearly illustrates the necessity of high energy resolution and
the resonance excitation energy in order to extract the reliable information of Ce 4f features near $E_F$ in the PES spectra [38].

To determine $U$ experimentally, the PES and IPES spectra of CeAg$_2$Ge$_2$ are shown in figure 2(a). Here, the transitions to the lowest final state of Ce are considered which correspond to the minimum energy required to excite a Ce 4f electron to $E_F$ ($\Delta_\gamma$) in the case of PES and the transition which corresponds to exciting an electron from $E_F$ to the first empty 4f state ($\Delta_\delta$) in the case of IPES. $U$ has been determined from the relation $U = \Delta_\delta - \Delta_\gamma$. The position of the features in PES and IPES spectra have been determined by fitting the spectra with the multiple Gaussian peaks as shown in figures 2(b) and (c). Minimum numbers of peaks are considered which provide a good fit. Background correction has been carried out by considering a Tougaard background [39] for PES spectra [10, 11] and a parabolic background for the IPES spectra [40]. In the IPES spectra in figure 2(c) the state which is lying near to the $E_F$ at 0.6 eV corresponds to $f^1$ configuration and the state at higher binding energy of 2.5 eV corresponds to $f^2$ configuration. The intermediate feature between $f^1$ and $f^2$ corresponds to Ce 5d states at 1.4 eV (figure 2(c)) [38, 41]. Similar assignment of $f^1$, Ce 5d and $f^2$ features have been shown for the $\gamma$-type Cerium and its compounds [38, 41]. However, for this system Ce features corresponding to the $f^2$ state is slightly at the lower binding energy as compared to Ce metal [38, 42] and other Ce alloys [43] probably due to the lower correlation energy and weaker hybridization present in this system. For Ce metal the correlation energy has been found to vary from 4 eV to 6 eV and depends on the position of the $f^1$ and $f^2$ features in the occupied and unoccupied electronic structure [15]. The suppressed $f^1$ feature is related to the magnetic nature of the $\gamma$-Ce [38, 42]. The position of the $f^1$ and $f^2$ features in the IPES spectra for this system is in good agreement with other Ce-based systems which show weak hybridization like CeGe$_2$ [42], Ce-Rh$_2$, CeSb etc [1]. The instrument used for the IPES measurement produced reliable data for the other systems like LaCoO$_3$, PrCoO$_3$, [40] $\alpha$ and $\beta$ Brass [44] and hence confirms the correctness of the IPES spectra for this system. The energy positions of the $f^0$ and $f^2$ features are $-1.7$ eV ($\Delta_\gamma$) and $+2.5$ eV ($\Delta_\delta$). So the value of $U$ determined from experiment is 4.2 eV. A similar method was employed to determine the value of $U$ for Gd and NiO from XPS and BIS spectra [32, 33].

In order to understand the character of the features observed experimentally, we have calculated the density of states (DOS) using the FP-LAPW method with different $U_{eff}$. For $U_{eff} = 0$, the DOS calculation is reported in our earlier work [10]. The broadened DOS for occupied and unoccupied part of $U_{eff} = 0$ are shown in figure 2(a). A standard procedure has been adopted to broaden the DOS [10, 11, 45, 46]. The occupied part has been broadened by adding the PDOS of Ce, Ag and Ge as shown in figure 3 after multiplying it with the photoionization cross-section at 80 eV [47]. Since the cross-section of the unoccupied part is not reported in the literature, so to broaden the unoccupied part the PDOS are added without considering the cross-section. The added DOS is then multiplied with the Fermi function at the measurement temperature and convoluted with a Voigt function. The full width at half maximum (FWHM) of the Gaussian component is taken to be the instrumental resolution in the PES and IPES measurement. The energy-dependent Lorentzian FWHM represents the lifetime broadening [10, 20, 46]. The inelastic background and the matrix elements are not considered. The calculated valence band for $U_{eff} = 0$ shows that the features corresponding to Ce 4f states which are of itinerant character lie at the $E_F$ where as those of the localised character lie at $-1.5$ eV (see figure 2(a) and figure 3(b)). The small changes in the calculated valence band feature are prominently visible mainly due to the high resolution (20 meV). The calculated valence band with the poor resolution (400 meV) doesn’t show any difference in the spectral shape (figure 4(c) of [10]) and is the main reason why the effect of the correlation has not been observed by us in the experimental PES spectra earlier [10, 11]. Also, it is very clear that $U_{eff} = 0$ does not explain the IPES spectra and hence there is a need to take into account a larger $U_{eff}$ in the DOS calculation. Hence in figure 3, the partial densities of states (PDOS) are shown for $U_{eff} = 0, 1, 4, 2.7, 3.4, 4, 4.2$ and 5.4 eV. In the experimental PES and IPES spectra of CeAg$_2$Ge$_2$ the dominant contribution mostly arises from the Ce 5d, Ce 4f, Ag 4d and Ge 4p states; hence the PDOS of these states are shown in figures 3(a)–(d) respectively. Since $U_{eff}$ is the energy required to transfer an electron

\begin{figure}
(a) shows the PES spectra at on-resonance ($h\nu = 121$ eV) and off-resonance ($h\nu = 80$ eV) and IPES spectra of CeAg$_2$Ge$_2$ compared with the calculated valence and conduction band (dashed lines) for $U_{eff} = 0$. The Ce 4f features are marked by ticks. (b) shows the PES spectra at off-resonance and on-resonance fitted with the Gaussian peaks. (c) shows the IPES spectra fitted with the Gaussian peaks.
within the same $f$ band hence with increasing $U_{\text{eff}}$ changes are observed mostly in the Ce 4$f$ states while the other Ce 5$d$, Ag 4$d$ and Ge 4$p$ states remain almost similar to $U_{\text{eff}} = 0$ case in the occupied part [10]. However, small changes in the PDOS of Ce 5$d$ and Ge 4$p$ with different $U_{\text{eff}}$ have been observed in the unoccupied part in figures 3(a) and (d) respectively. This is because the Ge 4$p$ and the Ce 5$d$ states are partially filled states and the major unfilled states lie in the unoccupied part. For $U_{\text{eff}} = 0$, the Ce 4$f$/PDOS exists mostly in the unoccupied part with a small contribution in the occupied part. To show the contribution of the Ce 4$f$ states for $U_{\text{eff}} = 0$ at the higher binding energy in the occupied part, we have multiplied Ce 4$f$ PDOS by 50 and shifted it by 10. It is shown in the figure 3(b) by dashed line. $U_{\text{eff}} = 0$ clearly shows that the Ce 4$f$ states at −1.5 eV (marked by tick in figure 3(b)) is hybridized with the Ce 5$d$, Ag 4$d$ and Ge 4$p$ states [10].

As $U_{\text{eff}}$ is increased in the DOS calculation (figure 3), it is observed that the quasiparticle peak corresponding to $f^1$ state near $E_F$ vanishes and Ce 4$f$ band shows a splitting in the occupied and the unoccupied part (compare figure 3(b) with figure 4(a) of [10]). The splitting or the gap between the Ce 4$f$ states in the occupied and unoccupied part increases with $U_{\text{eff}}$ as expected since the on-site Coulomb repulsion increases with the correlation energy [48]. The disappearance of the $f^1$ peak with higher $U_{\text{eff}}$ in the occupied part of the DOS can be explained as follows: Ce 4$f$ states are partially localized and partially delocalized (itinerant) type. So, GGA calculation gives the information of both the localized $f^0$ and the itinerant $f^1$ states. The correlation energy in GGA + $U$ causes progressive localization of the 4$f$ states and leads to the change of ground state from itinerant to localized; hence only localized $f^0$ state is visible in the DOS for higher $U_{\text{eff}}$. A similar kind of observation has been reported for other Ce-based systems like CeRhIn$_5$ and CeIrIn$_5$ [49]. It is well known that the $\gamma$ phase of Ce is magnetic with local moments and low hybridization as well as the bandwidth is small compared to the Coulomb interaction [9, 50]. So the GGA + $U$ calculation describes the $\gamma$ phase of Ce the best since the 4$f$ electron is localized. The local moments are arranged in a lattice and form a paramagnet in the $\gamma$ phase. On the contrary the $\alpha$ phase is best described by the GGA calculations, indicating that the 4$f$ bands are itinerant and no magnetic moment exists any more. It is well known that the DFT calculation gives the accurate ground state of the system but fails to generate the final state effects. The itinerant $f^1$ feature in the experiment is the final state effect while the localized $f^0$ feature depends on the ground state that determines the correlation energy present in the system. In the DFT-based GGA + $U$ calculation $U_{\text{eff}}$ is the input parameter which works like a scissor operator between occupied and unoccupied states and is used to generate the localized ground state which matches with the experiment. Hence we have calculated the DOS with $U_{\text{eff}} = 4$ eV and 4.2 eV near the experimental $U$ value. Comparing the experimentally determined $f^0$ (−1.7 eV) and $f^2$ (+2.5 eV) features (figures 2(b) and (c)) with the theoretically determined Ce 4$f$ feature for $U_{\text{eff}} = 4.2$ eV.

Figure 3. Partial DOS (PDOS) showing Ce 5$d$,(a), Ce 4$f$,(b), Ag 4$d$,(c) and Ge 4$p$,(d) states for CeAg$_2$Ge$_2$ calculated with different $U_{\text{eff}}$ varying from 0 to 5.4 eV. The dashed line in (b) shows the PDOS of Ce 4$f$ state for the $U_{\text{eff}} = 0$, multiplied by 50 and shifted by 10 for the clarity of presentation of the Ce 4$f$ state in the higher binding energy region.

Figure 4. Calculated valence band (VB) and conduction band (CB) with different $U_{\text{eff}}$. 
shows that the maxima related to the Ce 4f states appears at −2.3 eV in the occupied part and +2.4 eV in the unoccupied part of the DOS which are in fair agreement with experiment. The DOS for the occupied and unoccupied parts has been broadened to compare it with the experimental PES and IPES spectra as shown in figure 4. The interesting observation is that the calculated valence band with different $U_{\text{eff}}$ shows almost a similar kind of trend with very little changes observed for the feature near −2 eV. The change in the spectral shape in the occupied part is mainly due to the Ce 4f feature which is very narrow and localized (see figure 3). For $U_{\text{eff}} = 4.2$ eV, the FWHM of the Ce 4f feature is = 100 meV. Also in the valence band the narrow Ce 4f states are covered by the broad features of Ce 5d, Ag 4p and the Ge 4p states. In fact this could be the reason that it was difficult to infer the presence of correlation effect near the Ce 4f states. With further increase in $U_{\text{eff}}$, the 5d states are covered by the Ce 4f states and the interference effect which specifically contribute to the spectral shape of the feature at −1.7 eV. However, the contribution from the interference effect and the 4f states are mainly responsible for the change in the spectral shape near $E_F$. The single 4f peak for $\Delta = 0.19$ eV has been split into a two-peak structure for a higher hybridization of $\Delta = 0.5$ eV. For further higher $\Delta$ the 4f related feature shifts towards the $E_F$. Hence the effect of hybridization in this system without any $U_{\text{eff}}$ is more prominent in the energy range between −1.0 to $E_F$ (figure 6(a)) and also seems to alter the spectral shape of the feature at −1.7 eV. In figure 6(b) we have shown the valence band spectra simulated by keeping the parameters $\epsilon_f = −1.7$ eV, $\Delta = 0.19$ eV and varying $U_{\text{eff}}$ from 0 to 6 eV. The $\Delta = 0.19$ eV has been determined from the analysis of Ce 3d$_{5/2}$ core-level peak and is reported in our earlier work [10]. It is interesting to note that the changes in the total simulated spectra with the increase in $U_{\text{eff}}$ from 0 to 4 eV are mainly due to the 4f state in the valence band and the interference effect near the $E_F$. There is hardly any difference between the total spectra for $U_{\text{eff}} = 3$ eV and 4 eV except the feature at $E_F$ which is found to be suppressed for $U_{\text{eff}} = 4$ eV and is related to the interference between the 4f and the 5d states. With further increase in $U_{\text{eff}}$ up to 6 eV there are no changes observed in the simulated valence band spectra. Hence we conclude that the $U_{\text{eff}} = 4$ eV should be present in this system. In figure 6(c) we have shown the valence band spectra simulated by keeping the parameters $\epsilon_f = −1.7$ eV, $U_{\text{eff}} = 4.2$ eV fixed and varying the hybridization strength $\Delta$ from 0 to 2.5 eV. $U_{\text{eff}} = 4.2$ eV is the experimentally determined U. The observations are
similar to figure 6(a) but with a slightly less intensity of the interference process and the 4f states with the increasing Δ. In figure 6(d) the experimental spectra are compared with the simulated SIAM spectra for Uff = 4.2 eV and 0 with the Δ = 0.19 eV. Two main differences are observed for the simulated SIAM spectra. One is the FWHM which is found to be 0.17 eV higher for the Uff = 4.2 eV (FWHM = 1.12 eV) than the Uff = 0 (FWHM = 0.95 eV). Second is the features near EF which are mainly related to the 4f states and the interference process are found to be suppressed for Uff = 0. Hence, the determination of the features near EF and the interference process are found to be suppressed for Uff = 0. Hence, the determination of the features near EF in the experiment with high resolution photoemission is extremely important in estimating the correlation energy and the strength of hybridization in this system. We have obtained a very good agreement for the SIAM spectra generated with the experimentally determined values of U = Uff = 4.2 eV and the hybridization strength Δ = 0.19 eV. The calculated ground-state configuration is (0.000348, 0.992677, 0.006974) for \( f^0 \), \( f^1 \) and \( f^2 \) states respectively in this system and the \( f \) occupation number \( n_f = 1.0 \) which is similar to \( \gamma \)-type Ce [21, 51]. This further confirms the correctness of the experimentally estimated values of \( U \) and Δ. Hence, the SIAM picture presents a qualitative understanding of the shape of the valence band and the features near the \( E_F \) that largely depend on the correlation energy and hybridization of the Ce 4f states in this system.

4. Conclusions

In conclusion, the electron–electron correlation energy for CeAg2Ge2 has been determined experimentally from the IPES and high resolution PES and compared with the theoretical GGA + \( U \) calculation. In the PES valence band spectra the effect of correlation and hybridization of the Ce 4f states largely depends on the spectral shape. DOS calculation shows that the Ce 4f state in the occupied part of the valence band is very narrow and localized and is covered with broad Ce 5d, Ag 4d and Ge 4p states. Hence, experimental high resolution
in PES is extremely necessary for the analysis of the Ce 4f features and determination of correlation in this system. On the other hand, the conduction band measured with the IPES gives a clear signature of the presence of correlation in this system due to the fact that the DOS of Ce 4f state in the unoccupied part is much higher as compared to the occupied part. The estimated value of $U$ from experiment shows a good agreement with the theoretical $U_{eff}$ for this system. SIAM analysis confirms the correctness of the experimentally determined values of the correlation energy and the hybridization strength present in this system.

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