Electronic structure of the strongly hybridized ferromagnet CeFe$_2$

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We report on results from high-energy spectroscopic measurements on CeFe$_2$, a system of particular interest due to its anomalous ferromagnetism with an unusually low Curie temperature and small magnetization compared to the other rare earth-iron Laves phase compounds. Our experimental results, obtained using core-level and valence-band photoemission, inverse photoemission and soft x-ray absorption techniques, indicate very strong hybridization of the Ce 4$f$ states with the delocalized band states, mainly the Fe 3$d$ states. In the interpretation and analysis of our measured spectra, we have made use of two different theoretical approaches: The first one is based on the Anderson impurity model, with surface contributions explicitly taken into account. The second method consists of band-structure calculations for bulk CeFe$_2$. The analysis based on the Anderson impurity model gives calculated spectra in good agreement with the whole range of measured spectra, and reveals that the Ce 4$f$ - Fe 3$d$ hybridization is considerably reduced at the surface, resulting in even stronger hybridization in the bulk than previously thought. The band-structure calculations are ab initio full-potential linear muffin-tin orbital calculations within the local-spin-density approximation of the density functional. The Ce 4$f$ electrons were treated as itinerant band electrons. Interestingly, the Ce 4$f$ partial density of states obtained from the band-structure calculations also agree well with the experimental spectra concerning both the 4$f$ peak position and the 4$f$ bandwidth, if the surface effects are properly taken into account. In addition, results, notably the partial spin magnetic moments, from the band-structure calculations are discussed in some detail and compared to experimental findings and earlier calculations.

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I. INTRODUCTION

The 4$f$ states of rare-earth elements in solids usually retain free-ionic properties with a well-defined integer occupation number. However, there are also rare-earth compounds where the hybridization of the 4$f$ states with extended band states is important, in which case they may exhibit properties usually only found in actinide systems. In such systems, many unusual phenomena are typically observed, like for instance anomalously low saturation magnetization and Curie temperature $T_C$ (e.g., CeFe$_2$), intermediate valence (e.g., SmS), heavy fermion behavior (e.g., YbBiPt), or non-Fermi-liquid behavior (e.g., CeCu$_{6-x}$Au$_x$). Even more surprisingly, simultaneous magnetic ordering and superconductivity has been observed (e.g., CeCu$_2$Si$_2$). The superconductivity is un-
conventional, i.e., the order parameter suggests a d-wave superconducting state, as opposed to the conventional s-wave state. Finding a proper theoretical description of the 4f states in these compounds remains one of the major problems in condensed matter physics.

As for the photoemission spectroscopy (PES) studies of Ce compounds, it is widely believed that the spectra are well described by the single-impurity Anderson model (SIAM). Recently, however, it has been argued that systems, in which the Ce 4f states hybridize strongly with the other valence electrons, calculations based on density functional theory (DFT) may give an equally good, or even better description of the photo-emission spectra than the SIAM analysis, provided that surface effects are properly taken into account in the analysis. However, one should bear in mind that calculations based on DFT are not strictly applicable for excited state properties, instead the ground state properties, such as the magnetic moments of the ground state, which are typically the focus of these calculations. Nevertheless, the electronic structure given from such calculations are often compared with photoemission data and good agreement between experiment and calculations is frequently observed. In the limit of complete screening of the excited state, one would expect ground-state density functional calculations to be able to describe the spectra well.

CeFe$_2$ is thought to belong to a class of strongly hybridized systems. This compound shows ferromagnetism below $T_C = 230$ K with a saturation magnetization of $2.30 \mu_B$/f.u. Above $T_C$, the magnetic susceptibility follows the Curie-Weiss law with an effective moment of $7.4 \mu_B$/f.u. If one compares CeFe$_2$ with the other RE$_2$ compounds ($R$: rare earth elements), a number of anomalies in its physical properties can be observed. The lattice constant is much smaller than an interpolation using the lattice constants of the other RE$_2$ systems would suggest. Its Curie temperature is anomalously low: the other RE$_2$ compounds have Curie temperatures ranging from 596 K to 796 K. The saturation magnetization is unusually low compared to the other RE$_2$ compounds (2.93 and 2.90 $\mu_B$/f.u. for LuFe$_2$ and YFe$_2$, respectively). Moreover, even if only a small fraction of the Fe atoms are substituted for Al, the ferromagnetic ordering is destroyed, and the system becomes anti-ferromagnetic. In fact, even in pure CeFe$_2$, recent neutron scattering experiments have revealed strong competition between the ferromagnetic ground state and an antiferromagnetic ground state. Together, these facts suggest that the Ce 4f states in CeFe$_2$ hybridize strongly with the other valence electrons, notably the Fe 3d valence states. This hypothesis is further supported by the X-ray absorption (XAS) experiments by Croft et al.

In this paper, we present high-energy spectroscopic results on CeFe$_2$ including core-level x-ray photoemission (XPS), XAS, Ce 3d-4f and 4d-4f resonant PES, bremsstrahlung isochromat (BIS) and high-resolution ultraviolet photoemission spectroscopy (UPS) in order to elucidate the electronic structure of this system. In the case of Ce compounds with strongly hybridized 4f states, it has been pointed out that surface effects are extremely important in the interpretation of the spectra. Therefore, we have attempted to differentiate the electronic structure of bulk and that of surface for CeFe$_2$ in the analysis of the spectra. As will be further elaborated on in section II.C of this paper, electronic-structure calculations with the Ce 4f states treated as valence states give a good description of the magnetism in CeFe$_2$. It is of course highly interesting to assess the applicability of the same theory in describing also the photoemission spectra of CeFe$_2$, even though as noted these calculations are not strictly applicable for excited state properties. Very recently, Sekiyama et al. reported a high-resolution 3d-4f resonant photoemission study of the strongly hybridized system CeRu$_2$ and found that the Ce 4f spectra can be explained by band theory. In the following, we first attempt to describe the spectra in the framework of the SIAM and obtain a set of SIAM parameters. In the analysis, surface effects on the spectra are explicitly taken into account. Next, the bulk component of the valence-band spectra is compared with the density of states calculated using density functional theory. All DFT results presented here have been calculated within the local spin-density approximation (LSDA). The use of more recently developed generalized gradient functionals would not, however, alter any of our conclusions.

II. METHODS

A. Experiment

Polycrystalline samples of CeFe$_2$ were prepared by arc-melting the pure constituent materials. Subsequently, the samples were annealed at 750 °C for a week to obtain single phase samples. Magnetization measurements yielded the same $T_C$ as in the literature. The XPS spectra were taken with Mg K$_\alpha$ radiation ($h\nu = 1253.6$ eV) using a double-pass cylindrical-mirror analyzer, and the BIS spectra were obtained using a Pierce-type electron gun and a quartz crystal monochromator which was set at $h\nu = 1486.6$ eV. The Ce 4d-4f resonant PES measurements were done at beam-line BL-2 of SOR-RING, Institute for Solid State Physics, University of Tokyo. The Ce 3d-4f resonant PES and Ce 3d XAS data were taken at beam-line BL-2B of Photon Factory, High Energy Accelerator Research Organization. Photoelectrons were collected using a double-pass cylindrical-mirror analyzer in the resonant PES measurements. The XAS spectra were obtained by measuring the total electron yield using an electron multiplier placed near the sample. All measurements were done in the range 50-80 K, i.e., below the Curie temperature. In the case of the Ce 4d-4f resonant PES, additional measurements at room temperature, i.e., above the Curie temperature, were performed. The total energy resolution was $\sim$1.0 eV for XPS and
BIS, ~0.5 eV for Ce 4d-4f resonant PES, ~0.5 eV for XAS and ~1.0 eV for Ce 3d-4f resonant PES. The high-resolution UPS measurements were done around 17 K using a hemispherical analyzer and the He I ($h\nu = 21.2$ eV) and He II ($h\nu = 40.8$ eV) resonance lines. The energy resolution was ~25 meV for both photon energies. The binding energies were calibrated using Au evaporated on the samples. For XAS and Ce 3d-4f resonant PES, the photon energies were calibrated using the Cu 2p edge of Cu metal and the Co 2p peak of LaCoO$_3$. Clean surfaces were obtained by scraping the sample repeatedly, while maintaining the sample under ultra-high vacuum, with a diamond file prior to each measurement. Cleanliness of the surfaces was checked by the absence of O 1s and C 1s XPS signals from contaminants in the case of the XPS, XAS, BIS and Ce 3d-4f resonant PES measurements. In the case of the high-resolution UPS and Ce 4d-4f resonant PES measurements, cleanliness was checked by the absence of a O 2p feature which appears around 6 eV below the Fermi level ($E_F$).

B. Single-impurity Anderson Model

The SIAM calculations were made based on the variational 1/$N_f$-expansion method developed by Gunnarsson and Schönhammer. Here, we performed the calculations to the lowest order in 1/$N_f$, where $N_f$ is the degeneracy of the Ce 4f level and was taken to be 14. The f$^2$ configuration was also included in the calculation. The energy dependence of the hybridization matrix elements was taken from the off-resonant spectra, which approximately represent the Fe 3d partial density of states. The configuration dependence of the hybridization strength was also taken into account, and was chosen to be the same as that obtained for α-Ce by Gunnarsson and Jepsen. In the calculations, we divided the band continuum into discrete levels following Kotani et al. We further assumed that each spectrum was a superposition of two components which represent bulk and surface spectra. The weight of each component was treated as fitting parameters within a range consistent with the universal curve for the mean free path of photoelectrons.

C. Band-Structure Calculation

In the band-structure calculations presented here, we have used the full-potential linear muffin-tin orbital method (FP-LMTO). In this method, the Kohn-Sham equations are solved for a general potential without any shape approximation. The local (spin) density approximation (LSDA) in the Hedin-Lundqvist parameterization was used for the density functional.

In the FP-LMTO method, space is divided into non-overlapping spheres, so-called called muffin-tin spheres surrounding each atomic site, and an interstitial region. The basis functions used are energy independent Bloch functions, whose construction is different in the spheres and in the interstitial.

A basis function in the interstitial is defined by the Bloch function of solutions to the spherical Helmholtz equation with nonzero kinetic energy $\kappa^2$, or a linear combination of such solutions for different kinetic energies. The Fourier representation of this basis function is taken from the Fourier series of a function matching the basis in the interstitial region but not inside the spheres, a so-called pseudo-wave function, whose exact shape inside the muffin-tin sphere is of no importance for the final solution as long as it is continuous and differentiable at the sphere boundary and matches the true basis function in the interstitial.

Inside the spheres, where the charge density varies rapidly, the basis functions are Bloch functions of numerical radial functions times spherical harmonics. The radial part of a basis function is constructed from the numerical solutions $\phi_L(E_\nu, r)$ of the radial Schrödinger equation in a spherical potential at the fixed energy $E_\nu$, and their energy derivatives $\dot{\phi}_L(E_\nu, r)$. Here, the index $L$ stands for a collection of quantum numbers: the principal quantum number $n$, the orbital quantum number $l$, the magnetic quantum number $m$, and the kinetic energy $\kappa^2$.

The treatment of the entire basis set within one single energy panel allows all states, including the semi-core states, to hybridize fully with each other. Our method is linear, i.e., the basis functions are constructed by expanding around fixed energies $E_\nu$. The expressions for the crystal wave functions in the muffin-tin spheres are matched to the interstitial crystal wave function at the sphere boundaries so that the total crystal wave function becomes continuous and differentiable in all space. In the present calculation, the expansion in spherical harmonics was taken up to $l = 6$. For Ce, the 6s, 5p, 6p, 5d, and 4f orbitals were included in the basis set, with 5p as semi core. For Fe, we included the 4s, 4p and 3d orbitals, i.e., no semi-core state was used for Fe. Four $\kappa^2$-values were used in the calculation: -0.6 Ry and -0.1 Ry for the valence states, and -1.5 Ry and -1.0 Ry for the semi-core Ce 5p states, all with respect to the muffin-tin zero.

Reciprocal space was sampled with what would correspond to 1331 k-points in the full Brillouin zone (BZ) using special k-point sampling methods. The non-overlapping muffin-tin spheres were chosen as 21% and 17% of the unit-cell lattice constant for Ce and Fe, respectively. With this choice, 36% or the unit cell volume is in the interstitial region and the closest muffin-tin spheres are 3% from touching.

The experimental lattice constant was used in the calculations. Furthermore, the calculations were spin-polarized but the spin-orbit interaction was not included. This latter approximation will be commented on further in conjunction with presenting and discussing the results from the band-structure calculation.
III. RESULTS

A. Experiment

Fig. 1 shows the Ce 3d core-level XPS and XAS spectra. The XPS line-shape is a typical one for a strongly hybridized Ce compound, consisting of three peaks which correspond to the $3d^0 4f^0$, $3d^0 4f^1$ and $3d^0 4f^2$ final states in each of the $j=3/2$ and $5/2$ spin-orbit components. In the XAS spectrum, the main peaks are due to the $3d^0 4f^2$ final-state multiplet and the satellite structures ~5 eV above the main peaks are due to the $3d^0 4f^3$ final states. The rather distinct $4f^0$ peaks in the XPS spectrum and the $4f^1$ structures in the XAS spectra, together with the obscured $3d^0 4f^2$ final-state multiplet structures of the main XAS peaks, indicate strong hybridization of the 4f states with the valence band in this system. The XPS spectrum reflects the surface electronic structure because of the rather low kinetic energies of photoelectrons from the Ce 3d core level. A detailed analysis of this is given below.

The results of valence-band PES and BIS are shown in Fig. 2. The on- and off-resonance occurs, respectively, at $h\nu = 121$ and 114 eV (881 and 875 eV) correspond to Ce 4d-4f (3d-4f) on- and off-resonance, respectively. Solid curves show the difference spectra, which represent the Ce 4f component.

As seen from this figure, there is a large difference between the Ce 4f spectra obtained from the Ce 4d-4f and Ce 3d-4f resonant PES. While the former has a double-peak structure in the vicinity of -2 eV and near $E_F$, the latter is dominated by a single peak near $E_F$, implying stronger hybridization in the latter. This can be attributed to the difference in the surface sensitivity of the two spectra due to the different kinetic energies of photoelectrons. This also indicates that the Ce valency at the surface is closer to trivalent than it is in the bulk.

In Fig. 2 we also show the XPS spectrum of the valence band taken with Mg Kα radiation. Owing to the higher kinetic energies of photoelectrons, this spectrum is considered to be more bulk sensitive than the above PES spectra. Considering the photoionization cross-sections, the valence-band XPS spectrum should mainly reflect the Fe 3d partial density of states (DOS) with significant contributions from Ce 4f and Ce 5d. As seen in the figure, the XPS spectrum shows a line-shape similar to the off-resonance spectra of Ce 4d-4f and Ce
3d-4f resonant PES.

It is expected, that the BIS spectrum should also reflect the bulk electronic structure rather well. There is a peak near $E_F$ and a broader feature at $\sim 6\text{ eV}$. They originate mainly from the Ce 4$f$ states, although there are contributions from the Ce 5$d$ and Fe 3$d$ states, too. The peak near $E_F$ and the structure around $\sim 6\text{ eV}$ correspond to the 4$f^1$ and 4$f^2$ final states, respectively. The broad line-shape of the structure at $\sim 6\text{ eV}$ is due to the 4$f^2$ final-state multiplet. The strong intensity of the peak near $E_F$ again indicates strong hybridization of the Ce 4$f$ states with the valence states.

![FIG. 3. High-resolution UPS spectra of CeFe$_2$. Inset shows an enlarged view near $E_F$.](image)

Fig. 3 shows high-resolution UPS data. In this photon energy range, the cross sections of the Fe 3$d$, Ce 4$d$, and Ce 5$d$ states varies rapidly with photon energy. The relative cross-section of Ce 4$f$ to the other orbitals increases when going from $\nu = 21.2$ to $40.8$ eV while that of Ce 5$d$ rapidly decreases. Therefore the structure at $-(2 \sim 3)\text{ eV}$ which appears only in the $\nu = 40.8$ eV spectrum, originates from the Ce 4$f$ states, and corresponds to one of the double peaks in the Ce 4$f$ spectrum obtained by the Ce 4$d$-4$f$ resonant PES. This observation is also consistent with the fact that the 40.8 eV spectrum is surface sensitive, according to the “universal curve” of the mean free path of photoelectrons. In the near $E_F$ region, structures just below $E_F$ and at $\sim -0.3\text{ eV}$ are somewhat enhanced in the 40.8 eV spectrum. These structures originate from the Ce 4$f$ states and correspond to the tail of the Kondo resonance (possibly with unresolved fine structures due to crystal-field splitting) and the spin-orbit side band, respectively. These structures are also expected to be dominated by surface contributions.

B. Single-Impurity Anderson Model

The SIAM parameters obtained in our calculation are listed in Table I. Here, $\epsilon_f$ is the position of the bare 4$f$ level ($4f^1 \rightarrow 4f^0$ ionization level) relative to $E_F$, $U_f$ is the 4$f$-4$f$ on-site Coulomb energy, $U_{ff}$ is the 4$f$-core-level Coulomb energy and $V$ is the Ce 4$f$-valence-band hybridization strength, in accordance with the definitions in Ref. [7]. Using those parameters, the 4$f$ occupation number $n_f$ has been calculated and listed in the last column of Table I. Since we have fitted many different types of spectra using the SIAM shown in Fig. 4, many constraints have lead to a rather unique set of SIAM parameters.

In Fig. 3, comparison is made between the SIAM calculations and the experimental spectra. As seen, we obtain good overall agreement with all experimental spectra. The main discrepancy between the SIAM results and experimental spectra is found in the BIS spectrum (Fig. 3), where the position of the calculated $f^1$ peak is about 0.5 eV lower than in the experimental spectrum. Noticeable from this figure is also the large difference between the bulk and surface spectra obtained through the SIAM analysis. For instance, in the Ce 4$f$ spectrum obtained from Ce 4$d$-4$f$ resonant PES (Fig. 3), which is basically a double-peak structure, the relative strength of the two peaks is very different between the bulk spectrum and the surface spectrum. Similar differences in directly measured bulk- and surface spectra have previously been reported for Ce-metal [14] and can be explained as due to larger hybridization in the bulk.

![Table I. SIAM parameters for CeFe$_2$. $\epsilon_f$, $U_f$, $V$, and $U_{ff}$ are given in units of eV.](image)

|                | $\epsilon_f$ | $U_f$ | $V$   | $U_{ff}$ | $n_f$ |
|----------------|--------------|-------|-------|----------|-------|
| surface       | -1.8         | 6.4   | 0.23  | 9.7      | 1.0   |
| bulk          | -0.8         | 6.4   | 0.41  | 9.7      | 0.78  |
However, there are noticeable amplitudes of the $f^0$ and $f^2$ configurations also at the surface, indicating that also here, some hybridization between the $4f$ and valence states is taking place.

![Graphs showing CeFe₂ spectra](image)

FIG. 4. Comparison of the single-impurity Anderson model calculation with the experimental spectra of CeFe₂. (a) Ce $4f$ spectrum obtained from Ce 4d-4f resonant PES. (b) Ce $4f$ spectrum obtained from Ce 3d-4f resonant PES. (c) BIS spectrum. (d) Ce 3d core-level XAS spectrum. (e) Ce 3d core-level XPS spectrum. In each panel, dots show experimental spectrum, solid curve shows the calculated spectrum, and dotted and dash-dotted curves show the calculated surface and bulk components, respectively.

C. Band-Structure Calculation

Experimentally, the partial moments in CeFe₂ have been studied using several different experimental methods: polarized neutrons, Compton scattering, and, very recently, x-ray magnetic circular dichroism (XMCD). In all experiments, an anti-parallel coupling of the Ce and Fe moments is found. This coupling is also reproduced in our calculation, as well as in earlier calculations. As is well known, this anti-parallel coupling of the moments is a strong indication that the Ce $4f$ states in CeFe₂ are delocalized. This can easily be understood from the following argumentation. If the $4f$ electrons are localized, the $4f$ spin moment would be dictated by the polarization of the $spd$-electrons of the Ce atom, that via hybridization effects are known to be anti-parallel to the $3d$ moment of the Fe atom. Hence the spin moments of the Ce atom and the Fe atom are always anti-parallel, both in the localized and delocalized case. For localized $4f$ electrons, the $4f$ spin moment is accompanied by an orbital moment (larger than the spin moment) that (via Hund’s third rule) is anti-parallel to the Ce spin moment. Hence, for localized $4f$ electrons the total (spin+orbital) Ce-Fe coupling is ferromagnetic, whereas if the Ce $4f$ orbital moment is quenched, due to band formation, the coupling is anti-parallel.

In Fig. 5, the spin-resolved partial DOS for the Ce $4f$, Ce $5d$ and Fe $3d$ states are shown. The first and third panels show the majority spin channel for Ce and Fe, respectively, and the second and fourth panels show the minority spin channel. Comparing the DOS for Ce and Fe, we see that the Ce $4f$ and Fe $3d$ states have opposite spin polarization. Furthermore, the Ce $5d$ band width is seen to be much larger than that of the Ce $4f$ and Fe $3d$ states, with the magnitude of the Ce $5d$ DOS roughly an order of magnitude smaller than that of the Ce $4f$ and Fe $3d$ states.

Fig. 5 shows the band-structure of spin-polarized CeFe₂ along high-symmetry directions in the Brillouin zone. The flat bands clustered just above the Fermi level are predominantly of $4f$-character. In the region from $\sim$2 eV to $\sim$10 eV, and around -5 eV with respect to the Fermi level, the spin splitting of the bands is clearly visible.

Our calculated total spin magnetic moment amounts to 2.48 $\mu_B$ per formula unit (experimental saturation magnetization: 2.30 $\mu_B$, as stated earlier in this paper), with the main contributions being the Ce $4f$ moment -0.54 $\mu_B$, the Ce $5d$ moment -0.23 $\mu_B$, and the Fe $3d$ moment 1.75 $\mu_B$. The partial occupation numbers summed over spin, within the muffin-tin spheres, are 1.07 for Ce $4f$, 1.28 for Ce $5d$, and 6.18 for Fe $3d$. Note that the partial spin magnetic moments are calculated using the partial occupation numbers inside the muffin-tin spheres, which is somewhat arbitrary. The total spin moment is on the contrary, of course, well defined. An obvious point, which seems to have been overlooked so far, is that not only in band-structure calculations, but also experimentally, the division of space between individual atomic species in a compound is in fact not unique nor even well defined. It is reasonable to believe that different experimental procedures differ in their “volume of sensitivity” around each atom, and thus effectively correspond to different ways of dividing up the total space in the compound between the atoms. This could be one reason why different experimental techniques find quite different values for the partial magnetic moments, and also why, in order to find the total Ce moment from experimental results, assumptions have to be made regarding the ratio of the number of $5d$ and $4f$ electrons contributing to the magnetization.
An analysis of experimental data along this direction of thought might help resolve controversies regarding the electronic structure of CeFe₂.²³

A calculation of the moments including spin-orbit coupling and orbital polarization,³¹ using the FP-LMTO method, has been performed earlier by Trygg et al.¹³ The difference between the presently reported spin moments and the ones reported by Trygg et al.,¹³ which include spin-orbit coupling, is very small, around 1%. Thus, the effect of including spin-orbit coupling is shown to have only a very minor effect on the magnitude of the spin moment. Calculations by Eriksson et al.¹² using the atomic sphere approximation (ASA) give somewhat different values for the magnetic moments than the present method, in which no such geometrical approximation regarding the form of the potential, wave functions or charge density is made. As demonstrated in Ref.¹³, the spin density in CeFe₂ is highly non-spherical, which may well be the reason for the differences in results from full-potential and ASA calculations. To summarize, the arguments presented above justify our present calculational approach, i.e., using a full-potential method, but neglecting spin-orbit coupling.

Concerning the absolute magnitudes of the individual moments, the discrepancies between different experimental approaches can be quite large, for instance, the Ce 4f spin moment is measured to be -0.37 µB with XMCD, whereas polarized neutrons find the corresponding moment to be only about a fourth as large: -0.10 µB. As already touched upon above, one reason for these discrepancies between different experimental techniques may well be that they differ in the way the space in the compound is effectively divided up between the atoms. With this in mind, the magnitudes of our calculated moments must be said to be in satisfactory agreement with exper-
imental findings, although the overall trend appears to be that the calculations overestimate the moment magnitudes.

![Graph](image-url)

**FIG. 7.** Comparison of the DFT DOS with the experimental spectra. dot-dashed curves show orbital components. In the PES part, the Ce 4f spectrum obtained by Ce 3d-4f resonant PES is shown.

In Fig. 7, we compare the valence-band Ce 4f PES and BIS spectra with the DFT DOS. As mentioned earlier, the Ce 3d-4f resonant PES spectrum and the BIS spectrum are rather bulk sensitive, and thus it is relevant to compare these spectra with bulk DFT calculations. In the PES part of the spectra, comparison is made between the experimentally obtained Ce 4f spectra and the Ce 4f-projected DFT DOS. As for the BIS part, the Ce 4f, 5d and Fe 3d partial DOS have been added taking account of the atomic photoionization cross-sections. Agreement between experiment and theory is satisfactory almost to the same extent as in the SIAM calculation. In the DFT DOS, the structure around 6 eV in the BIS spectrum is of course not reproduced, since this structure corresponds to the 4f^2 final state, and thus is a purely excited-state property of the system. Furthermore, in the DFT calculation, the energy of the near E_F peak in the Ce 4f PES spectrum and also in the BIS spectrum is slightly higher than in the experimental spectra. Also, the intensity on the higher binding energy side of the PES spectrum is underestimated in the calculation. However, one should note that the relative intensities depend also on the transition matrix elements, which are not included in the DOS curves.

**FIG. 8.** Valence-band PES spectra of CeFe$_2$ taken at various photon energies compared with the Fe 3d partial density of states from the band-structure calculation. The DFT DOS has been broadened with the experimental resolution of the 114 eV spectrum.

### IV. DISCUSSION AND CONCLUSIONS

Generally, for any material, the surface electronic structure can differ substantially from the bulk one. For valence fluctuating systems like CeFe$_2$, it is very likely that the electronic structure of the Ce atoms close to the surface is not the same as that of the bulk Ce atoms. Therefore, in order to study the bulk electronic structure of valence fluctuating Ce compounds by means of high-energy spectroscopic methods, it is essential to take into account the effects of the sample surface when interpreting the spectra. In the present work, by assuming that the spectra are superpositions of the surface and bulk components, we have shown that all measured spectra of
CeFe₂ are fairly well reproduced by the SIAM calculations using the same set of parameters. At the surface, Ce is found to be nearly trivalent. The bulk set of parameters places CeFe₂ in the strongly intermediate-valent regime, giving a 4f-occupation number \( n_f \) as small as 0.78 (with considerable amplitude of the \( f^2 \) configuration both in the surface and bulk). This means that the Ce 4f states are strongly hybridized with the Fe 3d states in the bulk and that the states around \( E_F \) have a large amount of \( f \) character. Also, the differences between our SIAM-derived bulk- and surface spectra for CeFe₂ are similar to the differences between directly measured bulk- and surface spectra of Ce-metal, a difference which can be explained as due to larger 4f hybridization in the bulk than at the surface.

Apart from the SIAM analysis, a number of features of the measured spectra force us to draw the same conclusion regarding the nature of the 4f states in the bulk and at the surface, notably the large difference between the Ce 4f spectra obtained from the Ce 3d – 4f and Ce 4d – 4f resonant PES, and the strong intensity of the peak near \( E_F \) in the BIS spectrum.

As a result of the strong hybridization of the Ce 4f states in the bulk, the "f₀\(^{th}\)" final state feature in the Ce 4f spectrum deduced from the Ce 3d-4f resonant PES has a very weak intensity in contrast to the Ce 4d-4f resonant PES spectrum, where the \( f^n\)-final-state feature leads to the well-known double-peak structure. In such a case, i.e., where there is strong screening of excitations, it is expected that the bulk 4f spectrum can be interpreted in terms of a one-electron picture, and thus the DFT DOS should compare well with the 4f spectrum. This is also seen to be the case. Comparison of the 4f spectra with the DOS (Fig. 6) shows that the Ce 4f partial DFT DOS describes the valence-band Ce 4f spectra well, except for the \( f^2 \) structure in the BIS spectrum of course, since the \( f^2 \)-peak is due to incomplete screening. This fact poses the question of how the "f₁\(^{th}\)" final state (which is commonly referred to as the "Kondo peak") of the SIAM picture and "the 4f band" in the band picture are related to each other, since according to DFT, this peak is a one-electron feature, and in the SIAM, this is due to a many-body effect.

We also draw the conclusion that due to the strong hybridization in the bulk, the spin-orbit side band seen in the high-resolution UPS spectra (Fig. 3) must have surface origin since it is known that the spectral weight of the spin-orbit side band is strongly reduced when the hybridization is strong [4].

We now turn to a more detailed comparison of how well the DFT calculations and the SIAM analysis perform for the different spectra. Regarding the position of the near \( E_F \) peak in the BIS spectrum, the DFT calculation predicts a higher energy than experiment while the SIAM calculation predicts a lower energy than experiment. The intensity on the higher binding energy side of the near \( E_F \) peak in the PES spectrum is underestimated in the DFT calculation (although strictly speaking, intensities cannot be expected to be reproduced with a DOS, since the transition matrix elements are neglected) while it is overestimated in the SIAM calculation. The position of the near \( E_F \) peak in the PES spectra is calculated to be too close to \( E_F \) both in the SIAM and DFT calculations. As for the Fe 3d component, the DOS calculated using DFT does not give a good account of the intensity in the experimental spectra near \( E_F \). This may be due to that the 4f transition matrix elements are large close to the Fermi level compared to the 3d transition matrix elements.

All in all, the above discussion amounts to that the Ce 4f electrons in the bulk hybridize strongly with the Fe 3d electrons. This conclusion agrees perfectly with the experimentally observed anti-parallel coupling of the Ce and Fe moments, which is also reproduced in the DFT calculation. In the SIAM, the 4f electron is assumed to be localized, which indirectly implies that a parallel coupling of the Ce and Fe moments is expected.

Finally, we wish to mention some sources of error in the present work. Our measurements were done on scraped surfaces, which might make the surface rough, and therefore ill-defined. Furthermore, the precise values of photoelectron mean free paths are difficult to estimate, which naturally also has the effect of making the border between "bulk" and "surface" somewhat ill-defined. Our SIAM is not the most elaborate one, for instance we assume a degeneracy of 14 of the 4f level, thereby neglecting spin-orbit coupling and anisotropic hybridization effects, which leads to a crystal-field splitting. Furthermore, as in all DFT calculations, the functional used treats electron correlation only to a limited extent, i.e., it is not meaningful to expect perfect agreement between the DFT results and experiment.

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