k-resolved electronic properties of ternary heavy fermion systems

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(Received 8 June 1998)

Electronic and structural properties of the heavy fermion intermetallics $CePd_2Si_2$ and $CeNi_2Ge_2$ were determined using the techniques of low-energy electron diffraction, electron-energy-loss spectroscopy (EELS) and resonant photoemission. *Atomically clean* and *well-ordered* surfaces were prepared by evaporating the corresponding crystal onto a W(110) crystal. This preparation procedure allows the application of *angle-resolved* electron spectroscopic methods being sensitive to surface properties. The behavior of the rare-earth *f* states was determined by EELS. Resonant photoemission was carried out by tuneable synchrotron radiation allowing a direct assignment of the orbital nature of the electron states hybridizing in the valence band as well as to distinguish between states of the different constituents. [S0163-1829(98)02336-4]

In the last two decades the so-called heavy fermion systems[1–4] (HFS) attracted a growing interest in solid-state physics constituting a widely studied class of strongly correlated systems. These systems are binary or ternary compounds with lanthanides or actinides. Thermodynamic investigations of these materials result in properties at low temperature, which are described by a very high effective mass of the electrons. The reason of this feature lays in the high correlation of the *f* electrons with the conduction electrons in form of hybridization like the Kondo effect. While the thermodynamic investigations have more integral character, electron spectroscopic methods can principally offer a direct insight into the electronic properties.

Up to now, these surfaces were generally prepared by scratching with a diamond file or fracturing. Other techniques such as sputtering to noble gas atoms roughens the surface.

Angle-resolved photoemission is especially fundamental for the determination of electronic properties and in conjunction with tuneability of photon energy a direct assignment of the orbital nature of the states, which hybridize in the valence band can be obtained.[5,6]

In our study, we grow monocrystalline thin films of HFS material on a single crystalline surface. This preparation technique enables us to prepare *atomically clean* and *well-ordered* surfaces. We have chosen the ternary intermetallics $CePd_2Si_2$ and $CeNi_2Ge_2$, which were evaporated on a W(110) crystal. The film growth was investigated by means of low- and medium-energy electron diffraction (LEED, MEED) and Auger electron spectroscopy (AES). The electronic behavior of these high-quality films was determined using the technique of resonant photoemission. The giant resonance in the Ce 4*f* emission at 122 eV facilitated the determination of 4*f*-derived features in the photoelectron spectra[7] as well as to distinguish between the different hybridization characters of the bands involved in the bonding of the intermetallics. Electron-energy-loss spectroscopy (EELS) allowing dipole-forbidden *f*-*f* excitation was used to investigate the binding energies of the Ce 4*f* states due to the creation of a neutral excited state and thus avoiding a final ionic hole.

The experiment was performed in a UHV chamber with a base pressure below 2×10^{-11} mbar. It is equipped with a combined LEED–Auger system for surface characterization. A W(110) crystal served as substrate for the growth of the heavy fermion films. The crystal was cleaned in the usual way by heating in oxygen and flashing up to 2600 K. The films were evaporated by means of an electron-beam evaporator using crucibles with a melted $CePd_2Si_2$ and $CeNi_2Ge_2$ crystal inside, respectively. An integrated ionization-gauge-like flux monitor facilitated a reproducible evaporation rate. For the MEED measurement, the LEED system in combination with an external electron gun was used.

The electronic properties of the sample have been probed by the techniques of resonant photoemission, x-ray photoemission spectroscopy (XPS), and EELS. The energy distribution of the emitted and reflected electrons, respectively, is measured by a spectrometer system consisting of a cylindrical-mirror analyzer with sector field (300 mm slit-to-slit distance) with a high transmission. The energy resolution was set to about 150 meV. The angular resolution of the electrons was $\pm3°$. The stoichiometry of the ternary system was determined by means of XPS and AES. The primary energy of the EELS electron source can be varied between 5 and 300 eV. It contains a cylindrical-sector analyzer serving as *monochromator* of the electron beam. The energy width (full width at half maximum) can be reduced to below 50 meV independently of the primary energy. Magnetic fields were compensated to less than 0.1 μT by Helmholtz coils outside and screened by three layers of μ-metal foil inside the vacuum chamber. In the near future, spin analysis will be carried out by a SPLEED detector. Making use of the advan-
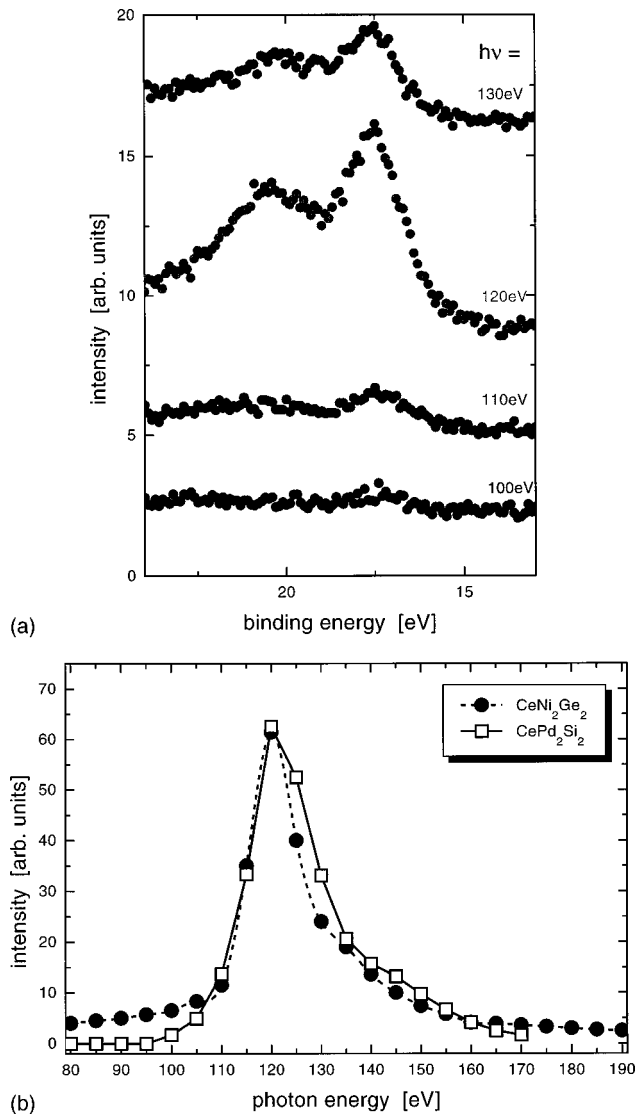
FIG. 1. (a) Energy distribution curves of $CePd_2Si_2$ showing the drastically enhanced emission of the Ce $5p$ states at an excitation energy of about 120 eV. (b) Peak intensities of the Ce $5p$ states as a function of photon energy for $CePd_2Si_2$ ($\square$) and $CeNi_2Ge_2$ ($\bullet$).

tages of tuneable excitation energy, photoemission measurements were carried out at BESSY, Berlin (SX700 monochromator).

The spectra of the energy region around 20 eV binding energy for excitation energies between 100 and 140 eV are shown in Fig. 1(a). Obviously, the emission of Ce $5p_{1/2}$ and $p_{3/2}$ is drastically increased at about 120 eV. This behavior is directly correlated with the onset of the resonant enhancement of the $4d \rightarrow 4f$ transition in the Ce compound. This process is described by $4d^{10}4f^15p^6 + h\nu \rightarrow 4d^94f^25p^6$ with subsequent $4d^94f^25p^6 \rightarrow 4d^{10}4f^15p^5 + e^-$.[8] The peak areas of the Ce $5p$-induced structures after a linear background subtraction were determined as a function of the excitation energy. This result is presented in Fig. 1(b) for $CePd_2Si_2$ ($\square$) and $CeNi_2Ge_2$ ($\bullet$). The giant enhancement of the cross section for a photon energy of about 120 eV is evident. The shape of these curves is in good agreement with theoretical calculations for metallic Ce.[9]

For photon-induced excitations, there is a giant resonance

in the Ce $4f$ emission at $h\nu = 122$ eV.[9] This behavior can be seen in Fig. 2 utilizing photon energies of 120 and 110 eV. This resonance was identified as a result from the transition $4d^{10}4f^1 \rightarrow 4d^94f^2$ followed by an Auger decay process $4d^94f^2 \rightarrow 4d^{10}4f^0 + e^-$, being a so-called "super-Coster-Kronig" transition.[8] Both spectra are normalized in such a way to give similar intensities in the energy region above 7 eV where no features are observed. The Pd-, Si-, Ni-, and Ge-derived photoemission intensities vary rather weakly with the photon energy. Therefore, by obtaining the difference spectrum, structures have to be Ce induced. The (120 −110 eV) difference spectrum is shown in Fig. 2(b) for $CePd_2Si_2$. The appearance of the peak near E_F is not a result of the subtraction procedure but is already seen in the 120 eV spectrum.

A prior investigation by Parks et al.[10] determined both features at 2 and 0.5 eV binding energy to be Ce $4f$ derived. In contrast, their sample was bulk material that was fractured and the measurement was carried out in an angle-integrated mode, thus only allowing the determination of the density of states but not k-resolved $E(k)$ behavior. Their difference spectrum only showed both features near E_F; the one at 5 eV with opposite sign was not detected. Therefore, the existence of this feature demonstrates the possibilities of angle-resolved investigations on high-quality and well-ordered surfaces. The corresponding investigation on $CeNi_2Ge_2$ [see Figs. 2(c) and 2(d)] does not show this structure. This directly points to a Pd-induced character. A possible explanation may be the $4d$ character of Pd valence-band electrons, in comparison to Ni $3d$, being involved into a d-f hybridization.

In order to get a further insight into the electronic behavior of heavy fermion systems, it is indispensable to investigate the orbital nature as well as the element character for the different states being involved into the bonding of the intermetallic. This determination was carried out for $CePd_2Si_2$ using photon energies between 75 and 150 eV. The photoelectron intensities were determined for the three peaks in the energy region near the Fermi level at binding energies at 0.5, 2, and around 5 eV (cf. Fig. 2). These values are shown in Fig. 3 ($\bullet$: 0.5 eV, $\blacklozenge$: 2 eV, $\blacksquare$: 5 eV). For excitation energies above 100 eV both peaks at low binding energy possess very low intensity and exhibit a giant enhancement at photon energies around 125 eV. This observation directly points to the f character of these electrons as already discussed above (cf. Fig. 2). The structure at a binding energy around 5 eV decreases slowly in intensity without any pronounced feature. Included into Fig. 3 are cross sections of Pd $4d$ states being experimentally determined[11] (dashed line) and theoretically calculated[12] (dash-dotted line), respectively. The shape of both curves is in good agreement to the intensity of the peak at 5 eV. This structure is therefore not caused by emission of Ce $4f$ states. Below an excitation energy of 100 eV the cross section of the peak at 0.5 eV increases not significantly to lower photon energies. As already observed for Ce $4f$ states,[13] this minimum is located around $h\nu = 100$ eV. Being in contrast, the structure at 2 eV increases rapidly to lower excitation energies. Below 100 eV the energy dependence of the cross section is therefore the same as for the 5 eV feature. This structure must therefore
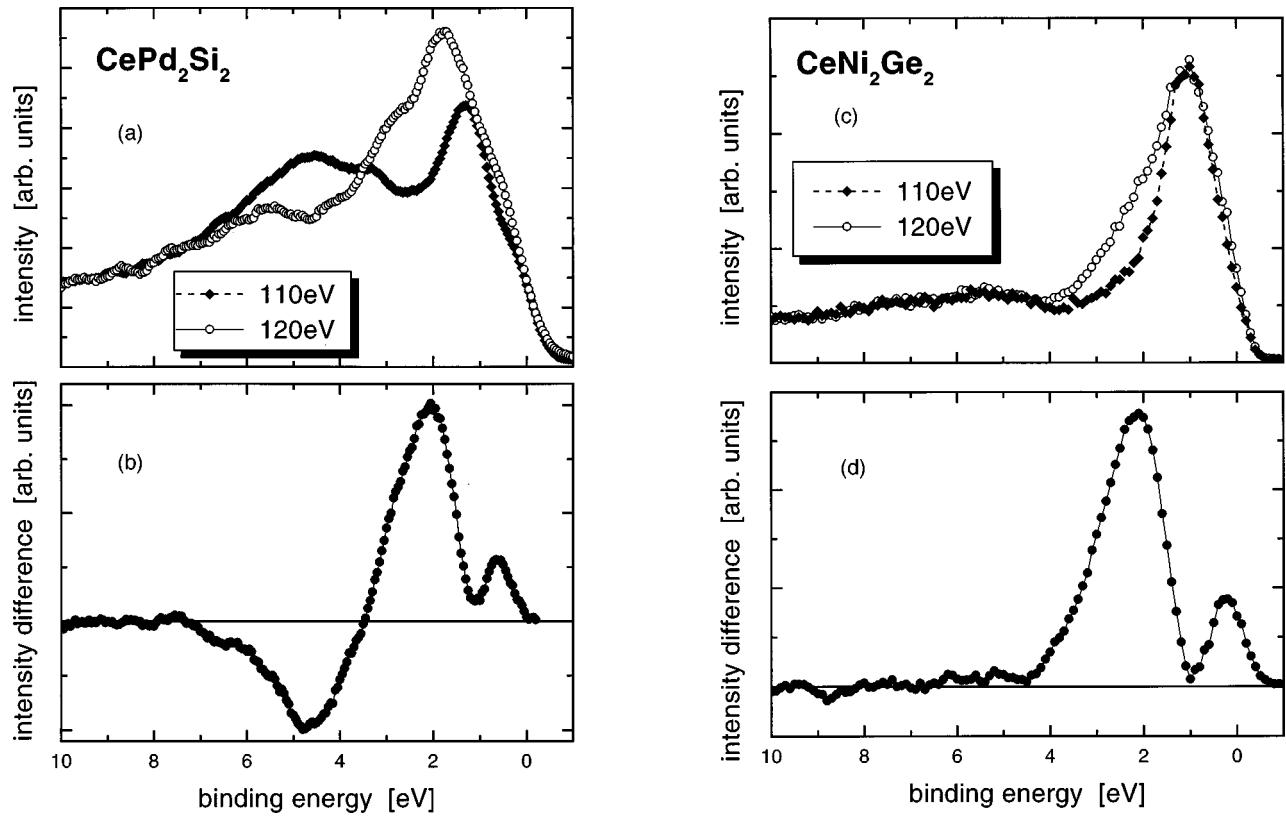
FIG. 2. Photoelectron spectra of $CePd_2Si_2$ (a) and (b) and $CeNi_2Ge_2$ (c) and (d). The spectra were taken at room temperature with an excitation energy of 110 and 120 eV. The difference spectra point to Ce $4f$ derived emission at a binding energy of 2.0 and 0.5 eV due to a giant resonance at about 120 eV.

arise from emission of a band being caused by orbital mixing due to a not significantly weighted hybridization of Pd and Ce states. The theoretical calculated photoionization cross sections of Ce $4d$ states[12] are shown as a dotted line. The shape of this curve with its maximum around $h\nu = 125$ eV demonstrates the f character of the photoemission peaks with binding energies of 0.5 and 2.0 eV.

EELS at low excitation energies is a surface sensitive technique to study the electronic structure by exciting collective oscillations or electrons from occupied into unoccupied states. In metals with a high density of states arising from d electrons, the excitation of plasmon losses has a relatively low probability. Therefore, the spectra are dominated by interband or intraband transitions. In rare-earth metals, excitations of the partially filled f shell are observed, that are assigned to be dipole-forbidden $4f$-$4f$ transitions. These transitions are enhanced near the $4d$-$4f$ threshold.[14]

Figure 4 shows a typical electron-energy-loss spectrum taken at a primary energy of the incident electron beam of $E_p = 27$ eV. Two characteristic features are present in the spectrum: a pronounced peak at 1.2 eV and a weak one at an energy loss between 2 and 3.5 eV. In comparison with band-structure calculations[15,16] and ultraviolet photoemission spectroscopy (UPS), the broad feature at about 2.5 eV can be assigned to be an interband transition. The loss at 1.2 eV represents a dipole-forbidden $4f$-$4f$ transition of the Ce compound. This value corresponds to the energy difference of the occupied and unoccupied $4f$ levels and gives evidence
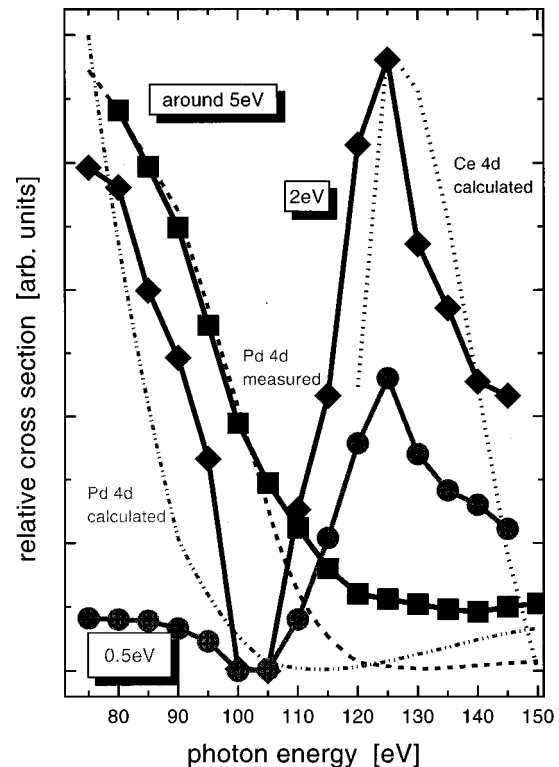

FIG. 3. Peak intensities of the three features near the Fermi energy for $CePd_2Si_2$ (●, ■, ◆). Included are relative cross sections for Pd $4d$ [calculated, dash-dotted (Ref. 12); measured, dashed (Ref. 11); and Ce $4d$ (calculated) dotted (Ref. 12)].
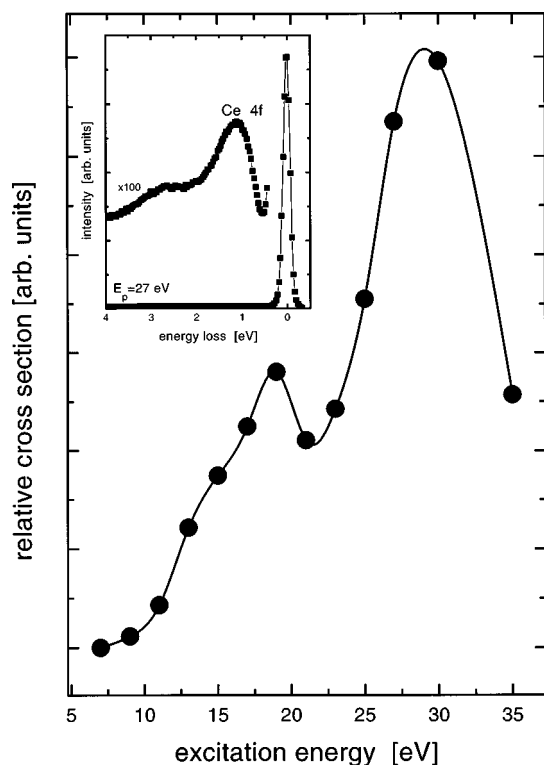
FIG. 4. Electron-energy-loss spectrum taken at room temperature with a primary energy of the incident electron beam of E_p $= 27$ eV; the prominent feature at a loss energy of 1.2 eV is caused by a dipole-forbidden $4f$-$4f$ transition of the Ce compound (see inset). The intensity of this feature is shown as a function of the electron excitation energy demonstrating a variation of the relative cross section.

for a $4f$ binding energy of below 1.2 eV. The final state in this excitation spectroscopy is a neutral excited state because no electron has been emitted. Therefore, the determination of

electronic properties of $4f$ states will be useful for a *direct* comparison with band-structure calculations for heavy fermion systems because in the photoemission process from a localized state an ionic final state is created due to the emission of the photoelectron. Thus, the final-state energy can be strongly shifted as compared with the neutral complex. As already shown in UPS and EELS investigations on rare earths (e.g., on Gd),[17] the binding energies determined by these techniques differ up to about 4 eV.

In summary we have determined structural and electronic properties of the Ce-based, ternary heavy fermion intermetallics $CePd_2Si_2$ and $CeNi_2Ge_2$ using the techniques of LEED, MEED, AES, EELS, and resonant photoemission. The atomically clean and well-ordered surfaces were prepared by metal beam epitaxy on a W(110) crystal. This preparation procedure enables the application of *angle resolving* electron spectroscopic methods being sensitive to surface properties of single crystalline material.

Using EELS, the binding energy of the Ce $4f$ states in this compound could be determined being important for theoretical work because by this excitation technique a neutral state is created in contrast to the remaining hole state in UPS. The giant resonance in the Ce $4f$ emission at 122 eV facilitated the determination of $4f$ derived features in the photoelectron spectra as well as to distinguish between the different hybridization characters of the bands being involved into the bonding of the intermetallics. In the future, the electronic properties will be determined below the characteristic temperature and additionally spin resolved in order to obtain further insight into the behavior of heavy fermion systems.

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