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Journal of Electron Spectroscopy and Related Phenomena 114–116 (2001) 693–698

**JOURNAL OF
ELECTRON SPECTROSCOPY
and Related Phenomena**

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Temperature-dependent bulk-sensitive Ce 3d edge resonant photoemission study of CeFe₂

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Received 8 August 2000; received in revised form 22 September 2000; accepted 29 September 2000

Abstract

We have performed temperature-dependent Ce 3d→4f resonant photoemission and X-ray absorption spectroscopy of CeFe₂ in ferromagnetic and paramagnetic phases with extremely high resolution (full width at half maximum (FWHM) < 100 meV). The on-resonance spectra show a typical two-peak structure which could not be observed in previous measurements with poorer resolution. The extracted Ce 4f spectral weights in both phases of CeFe₂ are quite well described by the Gunnarsson-Schönhammer calculation based on the Anderson single impurity model, but show big disagreement with the Ce 4f density-of-states obtained by band structure calculations. This indicates that the Ce 4f state in CeFe₂ has a fairly localized character. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Resonant photoemission spectroscopy (RPES); Anderson single impurity model (ASIM)

1. Introduction

Ce-transition metal (TM) intermetallic compounds show variety of physical properties and attracted considerable interest. When the energy position overlaps between the Ce 4f states and the more delocalized TM d states, strong hybridization between Ce 4f and TM d states develops and the ground state usually becomes α -like with non-mag-

netic ground state and high Kondo temperature. This can be qualitatively well understood within the framework of the Anderson impurity model [1–3]. However, among these Ce-TM compounds CeFe₂ is an exceptional case in that its ground state is ferromagnetic, and has been actively studied for that reason. CeFe₂ crystallizes in cubic Laves phase (C15) and orders ferromagnetically below 230 K (T_C). This Curie temperature is considerably lower than that for the isostructural compounds LuFe₂ ($T_C \sim 600$ K) with its full 4f shell and YFe₂ ($T_C = 545$ K) with no 4f electrons [4]. The saturation magnetic moment per formula unit of CeFe₂ $\sim 2.3 \mu_B$ is also significantly lower compared with $\sim 2.9 \mu_B$ for the other two compounds. Although it is agreed that

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most of magnetic moment per formula unit comes from Fe 3d states, band structure calculations predict Ce ions also carries non-negligible magnetic moment [5,6]. Hence 4f band magnetism was proposed for this material where ferromagnetically ordered Fe states induce an ordered 4f magnetic moment on Ce via strong hybridization between the Fe 3d and the (presumed) Ce 4f band. Several experiments utilizing neutron diffraction [7], X-ray magnetic circular dichroism [8,9], and Compton scattering [10] confirmed the existence of magnetic moments on Ce sites in the ground state of ferromagnetic CeFe_2 , although its magnitude is quite small and at variance among different experiments and theory. The existence of Ce moment, together with the fact that the lattice constant anomaly can be explained by the band theory, was claimed to be the proof that Ce 4f electrons in CeFe_2 form an itinerant band [5,6]. In the present work, we have performed combined Ce $3d \rightarrow 4f$ and $4d \rightarrow 4f$ resonant photoemission (RPES), X-ray photoemission spectroscopy (XPS) and X-ray absorption spectroscopy (XAS) with detailed analyses in both paramagnetic and ferromagnetic phases in order to understand the electronic structure and magnetic property of CeFe_2 . In particular, we tried to see whether the 4f-band theory or the Anderson impurity model better describes the electron spectroscopy data.

2. Experimental

Polycrystalline CeFe_2 sample was made by arc-melting stoichiometric mixture of Ce and Fe under the Ar atmosphere and annealing at 750°C , and the crystal structure was checked by X-ray diffraction pattern. Ce $3d \rightarrow 4f$ RPES and XAS at Ce $M_{4,5}$ edges were performed in the beamline BL25SU of SPring-8, Japan. The energy resolution of the photon source around Ce $M_{4,5}$ edge was better than 100 meV (full width at half maximum: FWHM) and the overall experimental resolution ~ 100 meV FWHM was obtained by Scienta SES200 electron analyzer [11]. The pressure in the vacuum chamber was below 5×10^{-10} Torr during the measurements. Temperature was controlled by closed-cycle He cryostat and a heater. The data were taken at about 20 K in ferromagnetic phase and 270 K in paramagnetic

phase. Sample surface was cleaned by filing with diamond file in situ and we checked the cleanliness of the surface by monitoring O 1s level. This cleaning procedure was repeated so that the O 1s core-level signal was kept below the detectability limit.

3. Results

Fig. 1 shows Ce 3d edge XAS spectra of CeFe_2 in both ferromagnetic (FM) and paramagnetic (PM) phases. We see two noticeable changes at different phases. One is the peak shape A and B in the $3d_{5/2}$ region. These peaks are known to come from the multiplet structure of the Ce $3d^9 4f^2$ final state, and it is generally observed that this multiplet structure is smeared out when there is strong hybridization effect between Ce 4f and band states, which reduces the Ce 4f electron count [12,13]. Hence the change of peak shape A and B indicates that the Ce 4f electron count is smaller in the PM phase compared with the FM phase. The other change to be noticed is the relative weight of peak C (C') in the Ce $3d_{5/2}$ ($3d_{3/2}$) edge

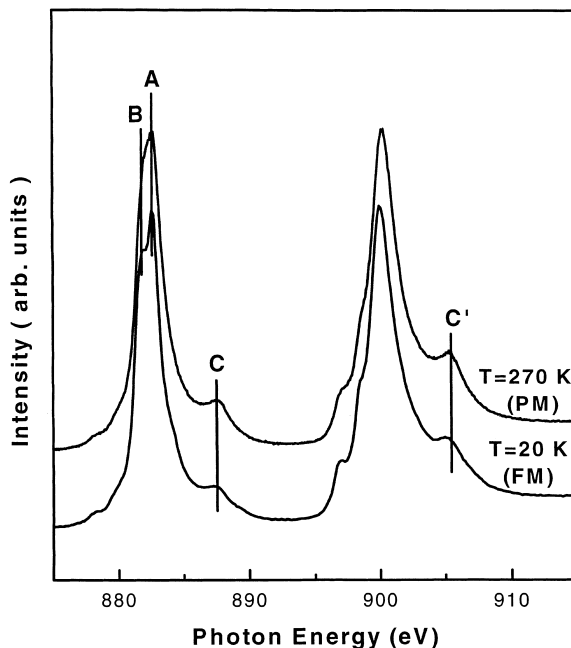
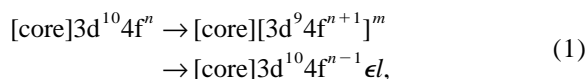


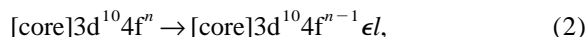
Fig. 1. Ce $M_{4,5}$ XAS spectra of CeFe_2 in both ferro- and paramagnetic phases.

region. This structure is known to come from the Ce $3d^9 4f^1$ final state, hence represents the amount of $4f^0$ state in the initial state [12,13]. The fact that the relative weight of C (C') is increased in the PM phase again indicates that the Ce 4f electron occupation number is decreased in PM phase compared with the FM phase. Hence we can conclude that Ce 4f occupation number is less in high temperature PM phase compared with low temperature FM phase in CeFe_2 . We also note that the distinct appearance of peak C (C') in the XAS spectra due to the configuration interaction between different Ce 4f valence states indicates fairly localized 4f character.

If we tune the incident photon energy to the peaks of Ce 3d XAS spectra, the Ce 4f electron emission is resonantly enhanced due to the transition $3d \rightarrow 4f$ followed by an direct recombination type Auger decay. The 4f emission results from the 'resonance' process



where ϵl , m refer to the continuum states and the different intermediate states, respectively. The final state in Eq. (1) is the same as for the 'direct' process



and the interference of the two processes have to be considered. We show such resonantly enhanced Ce 4f emissions in PM and FM phases of CeFe_2 in Fig. 2. Here we used the photon energy corresponding to the peak B ($h\nu = 881.9$ eV) of XAS spectra since spectra taken at higher photon energies are often found to be contaminated by incoherent Auger emissions [14]. In this case, the inset of Fig. 2 shows this phenomena, where arrows indicate contributions from Auger emissions. In Fig. 2, the Ce 4f spectral weights were extracted from Ce $3d \rightarrow 4f$ on-resonance spectrum by subtracting the off-resonance spectrum taken at photon energy below the absorption edge to remove contributions from non-Ce 4f states. This so-called resonant photoemission (RPES) technique has been extensively used to extract Ce 4f weights of many Ce compounds, but usually at lower photon energy Ce 4d edge [1]. The Ce 3d edge RPES shown here is different from Ce 4d RPES in that it is *bulk sensitive* [15], because the escape depth of a photoelectron is

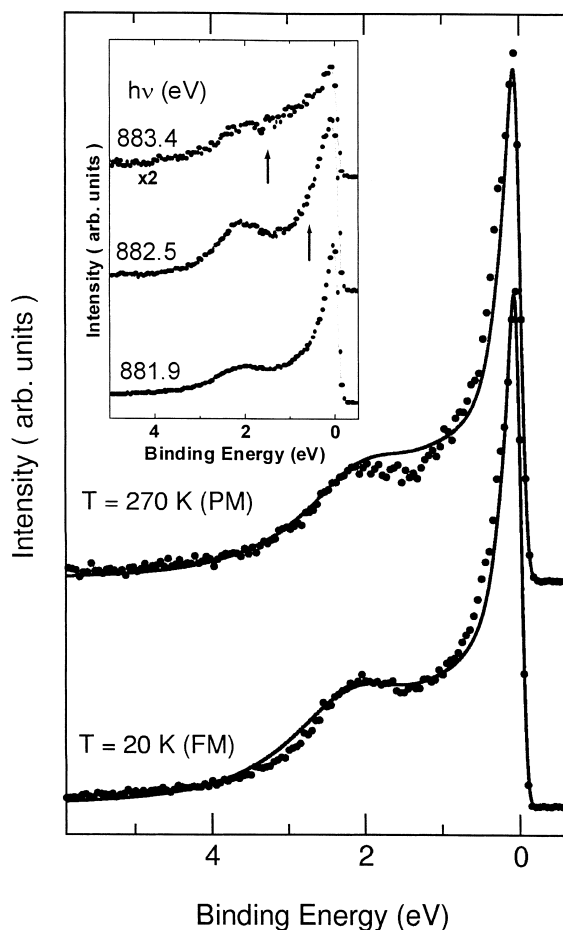


Fig. 2. Ce 4f spectral weights of CeFe_2 in both ferro- and paramagnetic phases. Dots are experimental data, and solid lines are fits from GS calculation based on Anderson impurity hamiltonian. The inset shows photoemission data at different photon energies, where we can see the contributions from Auger emissions (arrows) at higher photon energies.

larger than that of $4d \rightarrow 4f$ RPES due to the higher kinetic energy. These bulk-sensitive Ce 4f spectral weights in both phases show obvious two-peak structure which could not be observed in previous measurement with poorer resolution [16]. The peak around 2 eV is related to the f^0 final state and the peak near E_F can be assigned to Kondo tail. Although it is hard to see in the present figure, the relative peak intensity near E_F compared with the peak about 2 eV is slightly larger in paramagnetic phase at 270 K than in ferromagnetic phase at 20 K. Since the Kondo resonance should become smaller

as the temperature is raised [17], we believe this again implies stronger hybridization effect in the PM phase.

4. Discussion

To understand the electronic structure of CeFe_2 , we compared the extracted bulk-sensitive Ce 4f spectral weights both with band structure calculation and the Anderson impurity model calculation. Fig. 3 shows the comparison of the experimental Ce 4f weights in the FM phase (dots) with the Ce 4f density-of-states (DOS) calculated by either linear muffin-tin orbital (LMTO) method (dashed line) [18] or discrete variational method (solid lines) [19]. Theoretical densities-of-states were convoluted with the experimental resolution of 100 meV before comparison. We can see that both of these theoretical

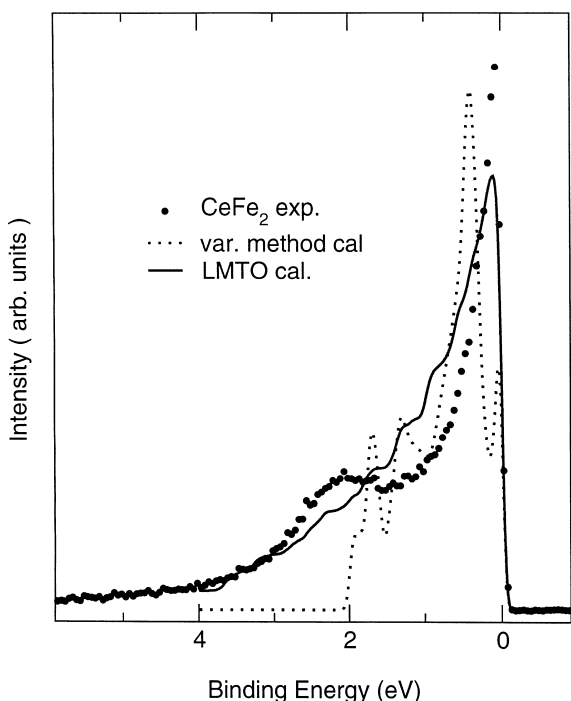


Fig. 3. The comparison of the experimental Ce 4f weights in the FM phase (dots) with the Ce 4f density-of-states (DOS) calculated by either the linear muffin-tin orbital (LMTO) method (dashed line) [18] or discrete variational method (solid lines) [19]. Theoretical densities-of-states were convoluted with the experimental resolution of 100 meV before comparison.

calculations show big discrepancies with the experimental data in terms of the width and peak position. Theoretical curve from discrete variational method has much wider width than the experimental 4f spectral weights and LMTO calculation shows the peak of 4f spectral weights ~ 0.4 eV below the Fermi level, while in the experimental curve the peak is right at the Fermi level within the experimental resolution. Furthermore, neither of them predicts a peak around 2 eV binding energy. Hence it is clear that one electron band calculations presently available fail to describe Ce 4f spectral weights of CeFe_2 obtained from Ce 3d RPES experiments.

We then analyzed the experimental Ce 4f spectral weights in ferromagnetic and paramagnetic phases by using the Gunnarsson-Schönhammer (GS) calculation based on the Anderson single impurity model (ASIM) [2,3]. Although strictly speaking the GS calculation is valid only at zero temperature, we assume it can still be applied in our case because the measuring temperatures are well below the expected Kondo temperature T_K . In paramagnetic phase (measuring temperature $T=270$ K), thermal broadening effect was included by convoluting Gaussian broadening factor into the theoretical curve. Since it is not simple to separate surface and bulk contribution from the experimental data, for the moment we neglect the surface effect for the bulk-sensitive 3d \rightarrow 4f RPES spectra. We showed in a previous publication that it is quite essential to employ realistic $V^2(\epsilon)$ in GS calculations in order to fully interpret experimental spectra [20]. Hence we used here the 3d \rightarrow 4f off-resonance spectrum taken at PM and FM phases, respectively, for the valence band shape to be hybridized with Ce 4f state. GS calculations include spin-orbit splitting of the 4f level. For basis states of GS calculation the lowest order f^0 , f^1 , and f^2 , and the second-order f^0 states are employed.

The results of the fitting with GS calculation are shown in Fig. 2 by solid lines super-imposed on the experimental data (dots). We can see that the GS calculations describe quite well the Ce 4f spectral weights of CeFe_2 in both phases. The used parameter values in ferromagnetic (paramagnetic) phase for fitting are as follows: The 4f-electron energy ϵ_f is -1.35 eV (-1.2 eV), the spin-orbit splitting of the f level Δ_{so} is 0.28 eV (0.28 eV), the hybridization

strength averaged over the occupied valence band Δ_{av} is 52 meV (47 meV), the on-site Coulomb interaction between 4f electrons U is 6.5 eV (6.5 eV). The Kondo temperature T_K expected from the GS calculation is 430 K (550 K), and the 4f-level occupancy number came out to be $n_f=0.88$ (0.85). We found that with these same parameter sets, we can also fit Ce 3d core-level photoemission data very well as shown in Fig. 4. These fitting results are also consistent with the XAS spectra of CeFe₂ shown in Fig. 1, where we have inferred that the n_f value is smaller in paramagnetic phase. The agreement between experimental data and GS calculation based on

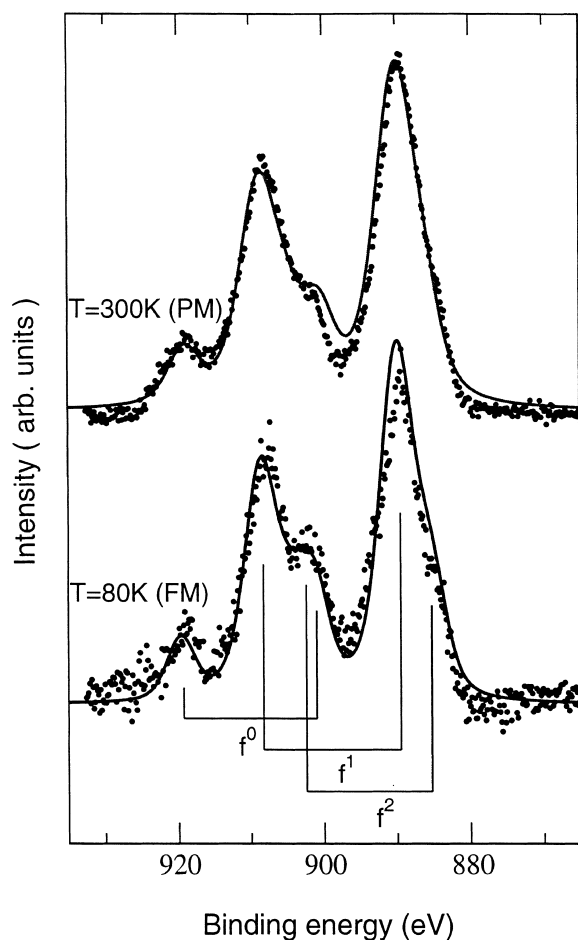


Fig. 4. Ce 3d core level XPS spectra of CeFe₂ in both ferro- and paramagnetic phases. Dots are experimental data, and solid lines are fits from the GS calculation based on the Anderson impurity hamiltonian.

ASIM implies that the Ce 4f ion retains fairly localized character, at least on the energy scale of photoemission spectroscopy.

Since the estimated Kondo temperature for Ce 4f electronic state ($T_K \sim 500$ K) is much higher than the Curie temperature ($T_C=230$ K) of CeFe₂, it is expected that Ce 4f magnetic moment is almost quenched even in the FM phase and its magnetic property is largely determined by Fe 3d electrons. This is consistent with the result of the neutron scattering experiment [7], where the magnetic moment of Ce ion is found to be much smaller than that of Fe. In addition, we can understand the reduction of Kondo resonance intensity in the FM phase compared with that in the PM phase observed in our experimental Ce 4f spectral weights of Fig. 2 from the result of the recent numerical renormalization group calculation [21], which predicts that Kondo resonance should be reduced in the presence of magnetic field.

5. Conclusions

We have studied the electronic structure of CeFe₂ by performing temperature-dependent bulk-sensitive Ce 3d→4f resonant photoemission and X-ray absorption spectroscopy with extremely high resolution (~ 100 meV FWHM) in both ferro- and paramagnetic phases. The bulk-sensitive 3d→4f on-resonance spectra of CeFe₂ with high resolution show typical two-peak structure in both phases. GS calculation based on ASIM describes well the Ce 4f spectral weights derived from 3d→4f RPES in both phases while the 4f density of states obtained from presently available one electron band calculations show big discrepancy, which implies that Ce 4f state in CeFe₂ has fairly localized character.

Acknowledgements

This work is supported by the Korean Science and Engineering Foundation (KOSEF) through the Center for Strongly Correlated Materials Research (CSCMR) at Seoul National University (2000) and BK 21 project of Ministry of Education, Korea. The authors thank Y. Saitoh, T. Muro, T. Matsushita, and

T. Nakatani for partial support for the experiments. This experiment was performed under the approval of the Japan Synchrotron Radiation Research Institute (1999B0104-NS-np).

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