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Spectroscopic evidence against Rh 4*d* itinerant ferromagnetism in $CeRh_3B_2$

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Valence-band photoemission and $L_{\rm III}$-edge x-ray absorption studies were performed on $R\rm Rh_3B_2$ (R = La, Ce, and Pr) compounds in order to explore the origin of the anomalously high magnetic-ordering temperature of $CeRh_3B_2$. From the low density of Rh 4*d* states at E_F and the approximate trivalency of Ce, itinerant magnetism in the Rh 4*d* band can be excluded. Instead, the magnetism is proposed to originate from Ce moments, enhanced by 4*f* hybridization with Rh *d* orbitals.

The ternary series of rare-earth (R) compounds, $R\rm Rh_3B_2$, crystallizing in the hexagonal $CeCo_3B_2$ structure, has recently attracted considerable attention due to the unusual magnetic properties of $CeRh_3B_2$ and $EuRh_3B_2$.[1-6] Both compounds order ferromagnetically ($T_c \cong 115$ K for $CeRh_3B_2$ and $T_c \cong 40$ K for $EuRh_3B_2$), even though Eu was reported to be in the trivalent, nonmagnetic ground state[7] and Ce in a mixed-valent state.[1] T_c of $CeRh_3B_2$ is the highest one reported for any Ce compound containing nonmagnetic constituents, and is also much higher than the ordering temperatures of the other $R\rm Rh_3B_2$ compounds, including $GdRh_3B_2$ (with $T_c \cong 90$ K).[3] These findings, together with the small ratio of the saturation moments to the effective moments, led several authors to claim that both $CeRh_3B_2$ and $EuRh_3B_2$ were itinerant-electron ferromagnets due to the Rh 4*d* band.[2-4,7] With this interpretation in mind, however, it is hardly understandable why the Rh 4*d* band should not induce itinerant magnetism in other members of this series, particularly in $LaRh_3B_2$ and $PrRh_3B_2$. In fact, $LaRh_3B_2$ is superconducting below 3 K, and $PrRh_3B_2$ orders ferromagnetically only below $T_c \cong 1.7$ K due to Pr local moments.[1] These discrepancies raise serious doubts on the validity of the itinerant-magnetism picture for $CeRh_3B_2$.

In the present paper we report on a comparative study of valence-band (VB) photoemission (PE) and $L_{\rm III}$-edge x-ray absorption (XA) spectra of $R\rm Rh_3B_2$ compounds (with R = La, Ce, and Pr), aimed at clarifying the origin of the anomalously high ferromagnetic-ordering temperature of $CeRh_3B_2$. The Rh-4*d*-derived VB PE spectra of all three compounds look essentially identical, with the Fermi level (E_F) situated in a region of low density of states. Thus the basic assumption for the occurrence of itinerant-electron magnetism in the Rh 4*d* band is not fulfilled in any of these compounds.[8] Instead, our observations strongly suggest the magnetism of $CeRh_3B_2$ to originate from a magnetic ordering of Ce moments. In consistency with this picture, the $L_{\rm III}$-edge data show that Ce is essentially trivalent in $CeRh_3B_2$, contradicting earlier conclusions based solely on the observed lattice volume anomaly.[1-4]

The PE experiments were performed with the SX-700 monochromator at BESSY (Berlin) employing a double-cylindrical mirror analyzer in an UHV chamber with a base pressure of 8×10^{-11} Torr. Clean sample surfaces were achieved *in situ* by scraping with a diamond file. $L_{\rm III}$-edge XA spectra were recorded at the EXAFS-II beamline at HASYLAB (Hamburg) using a Si(111)–double-crystal monochromator providing a rocking-curve width ≤ 2 eV [full width at half maximum (FWHM)] at $\cong 6$ keV. The compounds studied were synthesized by argon-arc melting of stoichiometric amounts of the constituent elements and characterized by x-ray diffraction and magnetic susceptibility measurements.

Angle-integrated VB PE spectra of the three compounds taken at $h\nu = 70$ eV are displayed in Fig. 1. At this photon energy the spectra are dominated by Rh-4*d* band emission, since the PE cross sections for other valence electron states are comparatively much smaller.[9,10] It is clear that the Rh 4*d* bands of all three compounds look essentially the same. We particularly note that in all three compounds E_F is located in a region of relatively low density of Rh 4*d* states [estimated to be ≤ 0.4 states/(atom/eV)]. This observation in fact excludes the concept of itinerant electron magnetism in the Rh 4*d* band of $CeRh_3B_2$, since a necessary condition in

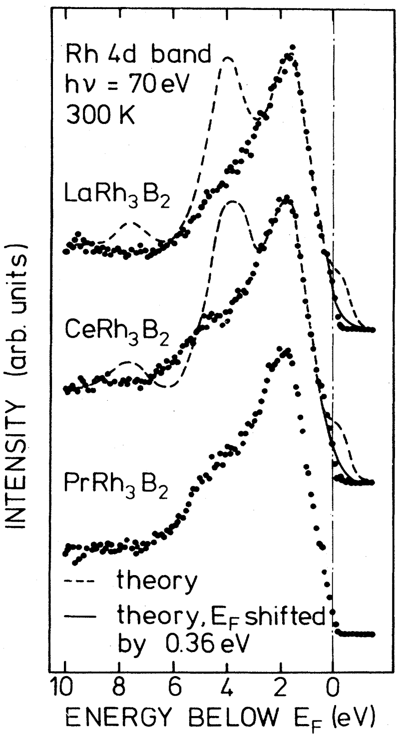

FIG. 1. Valence-band PE spectra of $LaRh_3B_2$, $CeRh_3B_2$, and $PrRh_3B_2$ at 70-eV photon energy, dominated by Rh 4*d* emission.

the Stoner-Wohlfarth theory of itinerant magnetism, i.e., a high density of states at E_F, is not fulfilled.[8] For comparison, the archetypical itinerant magnetic system $ZrZn_2$ features a high density of states at E_F.[8]

The spectra in Fig. 1 may also be compared with the recently calculated Rh $4d$ partial densities of states for $LaRh_3B_2$ and $CeRh_3B_2$.[6] To this end we have convoluted the theoretical density-of-states profiles from Ref. 6 with a Gaussian (0.8 eV FWHM) and superimposed them on reasonable integral background curves. The results are represented by the dashed lines in Fig. 1, where the prominent peak close to E_F has been lined up with the experimental spectrum. Obviously, the theoretical Fermi level has to be lowered in both cases by $\cong 0.35$ eV in order to match the experimental spectra. The second prominent peak in the theoretical Rh $4d$ density of states at $\cong 4$ eV below E_F is also observed in the VB PE spectra, but with much lower intensity. This is analogous to the case of Rh metal and has been explained as due to a strong decrease of the optical transition strength towards the bottom of the d band.[11]

We are therefore forced to attribute the origin of magnetism in $CeRh_3B_2$ to Ce $4f$ electrons. It should be mentioned here that a similar conclusion has been reached in Ref. 12 on the basis of magnetic studies of $La_xCe_{1-x}Rh_3B_2$ and $Ce(Ru_yRh_{1-y})_3B_2$. This concept, however, has to cope with the previous claim of an intermediate-valent state of Ce in this compound, based solely on the considerable lattice volume anomaly observed.[1,4] This prompted us to investigate this question[2] by the L_{III}-edge XA method. The room-temperature results are presented in Fig. 2, with identical spectra being observed at 77 K. As is well known, the L_{III}-edge XA spectra feature an edge structure plus an intense "white line" due to $E1$ transition of a $2p$-core electron into empty $5d$ states at E_F, with a high density of states. In intermediate-valent materials, a double-peaked white-line structure is generally observed caused by $2p^54f^n$ and $2p^54f^{n-1}$ final core states. The separation of the two peaks ΔE is given by the different Coulomb energies of the two final states and is typically 7–10 eV in the case of Ce compounds.

The principal features (A) of the three L_{III}-edge spectra in Fig. 2 are very similar, suggesting a valence state of Ce very close to 3. The solid lines represent the results of least-squares fits of a superposition of an arctan function (to simulate the edge) and a Lorentzian line, both convoluted by a Gaussian spectrometer function to the data points. As usual, a structure C due to scattering of photoelectrons is observed, which is of no relevance for the present discussion. In the spectrum of $CeRh_3B_2$, however, an additional weak structure B, $\cong 10$ eV above the main white line, is visible, indicating the population of the $2p^54f^0$ final state. A fit with a superposition of two L_{III}-edge profiles yielded the relative intensity of this $2p^54f^0$ component as $\leq 5\%$.

Feature B may be caused either by a $4f^0$ admixture to the ground state of Ce or by a shakeup channel originating from a trivalent Ce $4f^1$ ground state. An example for the latter situation was recently discovered in the case of divalent $EuPd_2P_2$ and interpreted as a consequence of a strong Eu-$4f$–ligand-orbital hybridization, presumably also giving rise to the lattice-volume anomaly in this compound.[13] We postulate an analogous mechanism for the present Ce compound. This view is supported by the results of recent electronic-structure calculations by Misemer, Auluck, Kobayasi, and Harmon for $CeRh_3B_2$, which reveal a consid-

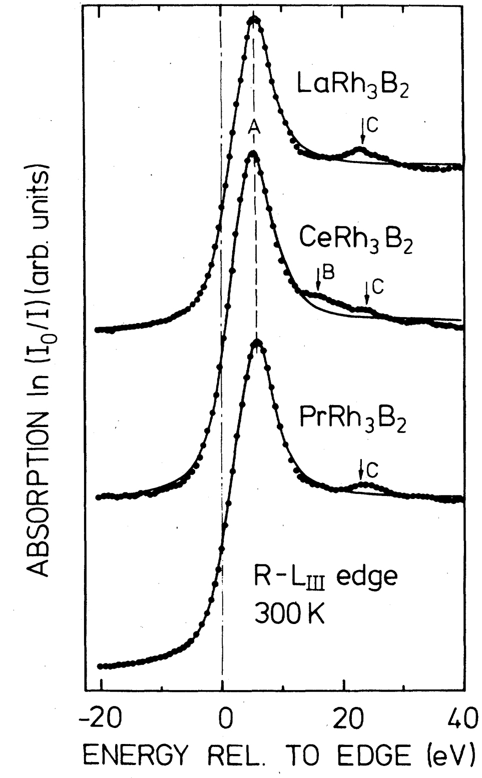

FIG. 2. L_{III}-edge profiles of $LaRh_3B_2$, $CeRh_3B_2$, and $PrRh_3B_2$. Zero represents the edge positions at 5485.6, 5722.2, and 5965.3 eV, respectively.

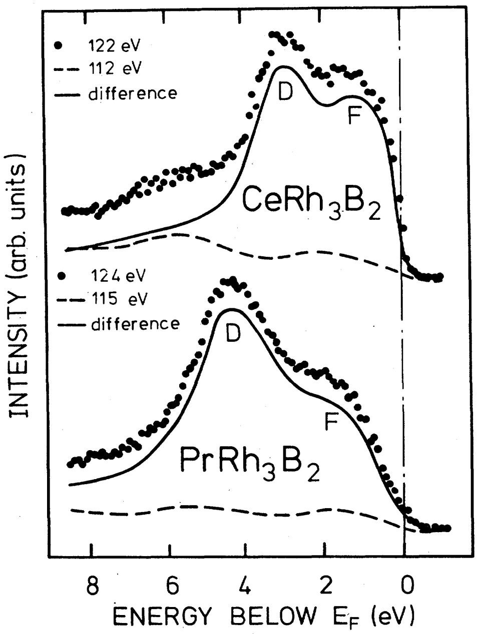

FIG. 3. Valence-band PE spectra of $CeRh_3B_2$ and $PrRh_3B_2$ taken "on" (full circles) and "off" (dashed curves) the $4d$-$4f$ resonances. The difference spectra represent the $4f$ emission.

erable hybridization between the occupied Ce 4*f* and the Rh 4*d* states.[6]

We have also investigated the 4*f*-derived PE spectra of these compounds employing the method of resonant PE.[14] The spectra "on" (data points) and "off" (dashed lines) the giant $4d \rightarrow 4f$ resonance are displayed in Fig. 3 for $CeRh_3B_2$ and $PrRh_3B_2$. At these photon energies, the Rh 4*d* PE cross section is in a Cooper minimum, so that contributions from Rh 4*d* states are very small. The difference spectra (full lines) obtained by subtracting photon-flux normalized off-resonance from the respective on-resonance data, represent 4*f* emission. In both cases a double-peaked 4*f* structure is observed, which is typical for Ce systems,[9,14,15] but has recently also been found for some Pr and even Nd systems.[14] While the overall intensity of 4*f* emission increases from Ce to Pr, as expected from an increasing 4*f* occupancy in the ground state, the relative intensity of peak *F* decreases in the same direction. Also, the separation of the two peaks increases slightly from Ce ($\cong 2.0$ eV) to Pr ($\cong 3.0$ eV), as well as the distance of peak *F* from E_F.

The long-standing controversy on the origin of the double-peaked structure in the 4*f*-derived PE spectra of Ce compounds—many-body ground state against final-state screening effects—has recently been settled in favor of the latter by the total-energy electronic-structure calculations of Norman *et al.*[15] These authors were able to show in a convincing way that peak *D* (see Fig. 3) is due to *d* screening of the *f* hole (poorly screened), while peak *F* is caused by *f* screening (well screened). The relative intensity of the *f*-screened peak is expected to increase with increasing 4*f*/valence-electron hybridization strength,[16] i.e., in agreement with observation in the direction from Pr to Ce.

This information sheds some light on the puzzling question, why T_c of $CeRh_3B_2$ is so much higher than that of $PrRh_3B_2$, and even of $GdRh_3B_2$. We suggest that the answer lies in the degree of hybridization of 4*f* electrons with Rh 4*d* orbitals, in addition to the size of the local 4*f* moment. The situation seems to be optimal in $CeRh_3B_2$. Our model would also explain the sizeable lattice-volume anomaly observed for $CeRh_3B_2$. Since the Rh atoms are arranged in a layer perpendicular to the *c* axis, a strong 4*f*/Rh 4*d* hybridization is expected to lead to a shrinkage of the lattice parameter *c*, whereas the basal-plane parameter *a* should follow the normal lanthanide contraction expected on the basis of essentially trivalent Ce, as observed earlier.[1]

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