Pressure-induced phase transition in $LaCo_5$ studied by x-ray emission spectroscopy, x-ray diffraction, and density functional theory

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The pressure dependences of the electronic and crystal structures of $LaCo_5$ have been studied with high-resolution x-ray absorption spectroscopy (XAS) and x-ray diffraction comprehensively. The lattice constant ratio of a/c shows an anomaly around 12–18 GPa without change in the lattice symmetry. In the XAS spectra with partial fluorescence mode as well as in the integrated absolute difference values of the Co $K\beta$ emission spectra, a change in the electronic structure was found at around a similar pressure range as the lattice constant anomaly. Density functional theory calculations confirm the presence of a magnetic anomaly around the same pressure region. No temperature dependence of the electronic structure for $LaCo_5$ and YCo_5 was observed.

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Quantum phase transitions can be classified into two categories. One is the conventional phase transition including some universality classes of ferromagnetic and antiferromagnetic transitions, transition to superconductor, and so on, which have been extensively studied so far in condensed matter physics. The other one is the topological phase transition without breaking spontaneous spin symmetry and changing the topology of the Fermi surfaces [1]. An example of the topological transitions would be metal-insulator transitions. In 1960 Lifshitz theoretically demonstrated another possible example of topological metal-metal transition or Lifshitz transition [2]. The Lifshitz transition occurs in noninteracting fermion systems and is characterized by the topological change of the Fermi surface without a magnetic transition. The Lifshitz transition is a typical continuous quantum phase transition and has been studied extensively for several decades both theoretically and experimentally.

However, the Lifshitz transition has attracted less attention compared to the conventional phase transitions because the topology of the Fermi surface is well defined only at $T = 0$ K in the original sense of noninteracting fermions. At higher temperatures the transition is thought to be smeared out. Recent theoretical studies renovated our view, showing a possible merging of the topological transitions and the conventional phase transition with the spontaneous symmetry breaking at a finite temperature, called a marginal quantum critical point [3,4]. If an actual measurement is performed at finite temperatures we cannot ignore the interaction between the fermions. It is physically important to make clear such a topological transition experimentally. Furthermore, Lifshitz transitions are interesting because the topological transition of the Fermi surface results in a van Hove singularity in the density of states at the Fermi level, inducing an anomaly in the free energy and anomalous physical quantities.

In general the Lifshitz transition is not a phase transition of the first or even second order but rather of the order of $2\frac{1}{2}$ [5]. However, Lifshitz also pointed out the existence of the first order phase transition as an exceptional case [2]. In order to experimentally study the Lifshitz transition, here we examine magnetic $LaCo_5$ and YCo_5. In YCo_5, pressure induces a first-order-like change in the volume without change in the lattice symmetry [5–7]. Rosner *et al.* suggested that the lattice collapse in YCo_5 was driven by magnetic interactions and could be characterized as the first-order Lifshitz transition [6]. Some band calculations have been performed for $LaCo_5$ and YCo_5 [5,6,8–10], however, no measurement of the electronic structure under pressure has been reported so far. In RCo_5 (R = rare earth) $LaCo_5$ and YCo_5 may be suitable systems to study the Lifshitz transition because the magnetic interaction between Co and La/Y is not significant and no strong local moment exists on La and Y.

A change in the Fermi surface can be measured by angle resolved photoelectron spectroscopy (ARPES). However, ARPES cannot be applied under pressure. X-ray emission spectroscopy (XES) on the other hand allows us to examine the electronic structures without the limitation to ambient pressure [11,12]. In our study therefore, we will employ Co $K\beta$ XES and x-ray absorption spectroscopy with partial fluorescence mode (PFY-XAS) under pressure. PFY-XAS is advantageous because a higher resolution compared to normal XAS can be achieved [12–14]. The $K\beta$ XES spectrum consists of the main spin-down and satellite spin-up components which allows us to observe the pressure-induced change in the electronic structure as well as the change in the

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spin states [15–17]. As the Lifshitz transition should not be accompanied by the crystal structural transition, we also performed x-ray diffraction under high pressure to confirm this. These methods will provide us with precise quantitative and qualitative information about changes in the electronic structure under pressures and its correlation to the volume change. Density functional theory (DFT) calculations are also performed to interpret the experimental data. Present results shine fresh light on the subject of the pressure-induced phase transition in $LaCo_5$.

Polycrystalline samples of $LaCo_5$ and YCo_5 were prepared by arc melting and subsequent annealing. Pure elements of La (99.99% pure), Y (99.99%), and Co (99.9995%) were melted with an arc furnace under argon atmosphere. The melted ingots were wrapped with tantalum foil and sealed in quartz tubes under vacuum. The ingots were then homogenized at 1323 K for 12 days and were quenched into water. For both XRD and XES measurements under high pressure, these samples, with dried KCl as the pressure medium, were loaded into a sample chamber of the gasket due to their chemical reactivity with pressure mediums such as methanol-ethanol mixtures or silicone oil. The nonhydrostaticity due to the use of KCl possibly makes the phase transition gentle at high pressures. Pressure was monitored using the ruby fluorescence method. Pressure dependence of the x-ray diffraction patterns were measured at BL12B2, SPring-8, using a 3-pin plate diamond anvil cell (DAC, Almax Industries) with a CCD detection system at room temperature. We took an arrangement of both incoming and outgoing x-ray beams of $h\nu = 20$ keV passing through diamond. The two-dimensional image of the CCD system was integrated by using the FIT2D program [18].

The PFY-XAS and XES measurements were performed at the Taiwan beamline BL12XU at SPring-8. The undulator beam was monochromatized by a cryogenically-cooled double crystal Si(111) monochromator. A Johann-type spectrometer equipped with a spherically bent Ge(444) analyzer crystal (radius of ∼1 m) and a Si solid state detector were used to analyze the Co emission of the $3p \rightarrow 1s$ de-excitation at the Co K absorption edge. In XES, high-pressure conditions were achieved at room temperature using a DAC coupled with a gas membrane.

Figure 1(a) shows x-ray diffraction patterns of the $LaCo_5$ powder sample under pressure up to 28.6 GPa. The diffraction patterns exhibited the $CaCu_5$-type crystal structure with a space group of $P6/mmm$. No structural transition is observed in the experimental pressure range. Figure 1(b) shows the pressure dependence of the lattice constants. Pressure-induced changes in the volume and the lattice constant ratio of a/c are shown in Fig. 1(c). The results indicate that there is a change in the trend of pressure evolution around 10–19 GPa. This anomaly is observed more clearly in the pressure dependence of a/c ratio in the volume range of 81–85 $\mathring{A}^3$ in Fig. 1(d), corresponding to the pressure range of around 12–18 GPa. The results agree with the c-axis anomaly and the flattening of the c/a ratio observed recently at 10–12.5 GPa in $LaCo_5$ [7]. An anomaly of the c/a ratio observed in the isostructural compound of YCo_5 was steplike [5,6], which is much more pronounced compared with $LaCo_5$.

Since a signature of the Lifshitz transition is the changes to the topology of the Fermi surface, it is important to measure the pressure-induced change in the electronic structure. Figure 2(a) shows the pressure-induced change in the PFY-XAS spectra of $LaCo_5$, where the emitted photon energy was set to the Co $K\beta_{1,3}$ peak. An expanded view around the prepeak is shown in Fig. 2(b). The prepeak of the XAS spectra consists of two components at 7711 and 7715 eV. On the other hand, the normal XAS spectra showed a shoulder peak [19]. The peak values at 7711 eV change clearly between 11.9 GPa and 15.0 GPa, which is the same pressure range where the anomaly of the lattice constant ratio is observed. We fit the PFY-XAS spectra assuming some peaks with Voigt functions and an arctan-type background for simplicity as shown in an example in Fig. 2(c). The resultant fits are shown in Figs. 2(e) and 2(f). The peak intensity and the peak energy change the trend around the same pressure range where the anomalies in the pressure dependence of the a/c ratio and the volume were found.

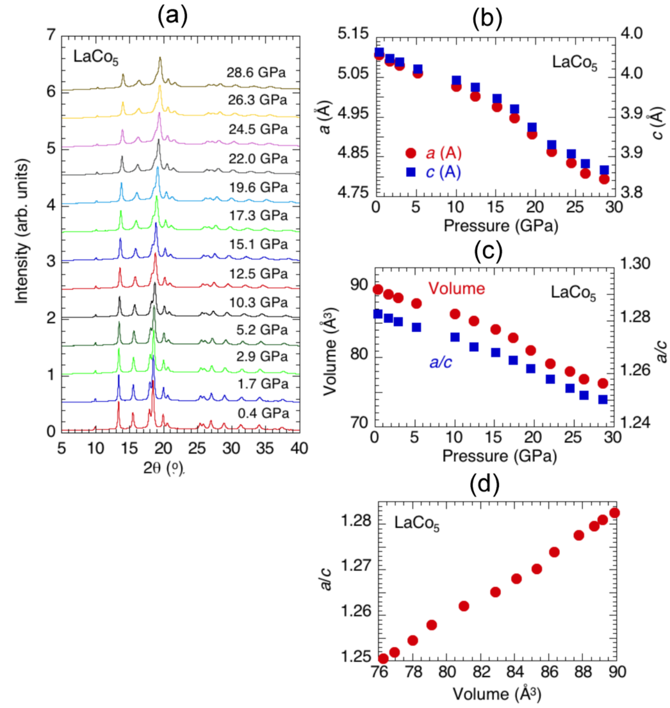

FIG. 1. Pressure dependence of (a) x-ray diffraction patterns, (b) lattice constants, and (c) volume and ratio of a/c for $LaCo_5$. In (d) dependence of the a/c ratio on the volume is shown.

Figure 2(f) shows pressure-induced change in the Co $K\beta$ XES spectra at $h\nu = 7760$ eV. The integrated absolute difference (IAD) of each spectrum at given pressure for a spectrum at 30.1 GPa was estimated as shown in Fig. 2(h) [17]. The IAD values decrease with pressure, indicating the change in the spin state from a higher-spin towards a lower-spin state. Although the pressure-induced changes in the IAD values are less sensitive compared to that in the PFY-XAS spectra, a change in trend seems to exist around the pressure where the anomaly of the a/c ratio was observed.

In general, pressure reduces the magnetic moment and changes the spin state from higher to lower states. In RCo$_5$ Co atoms occupy different sites with $2c$ and $3g$ symmetry. In YCo_5 the Co atoms on the two nonequivalent sites have the

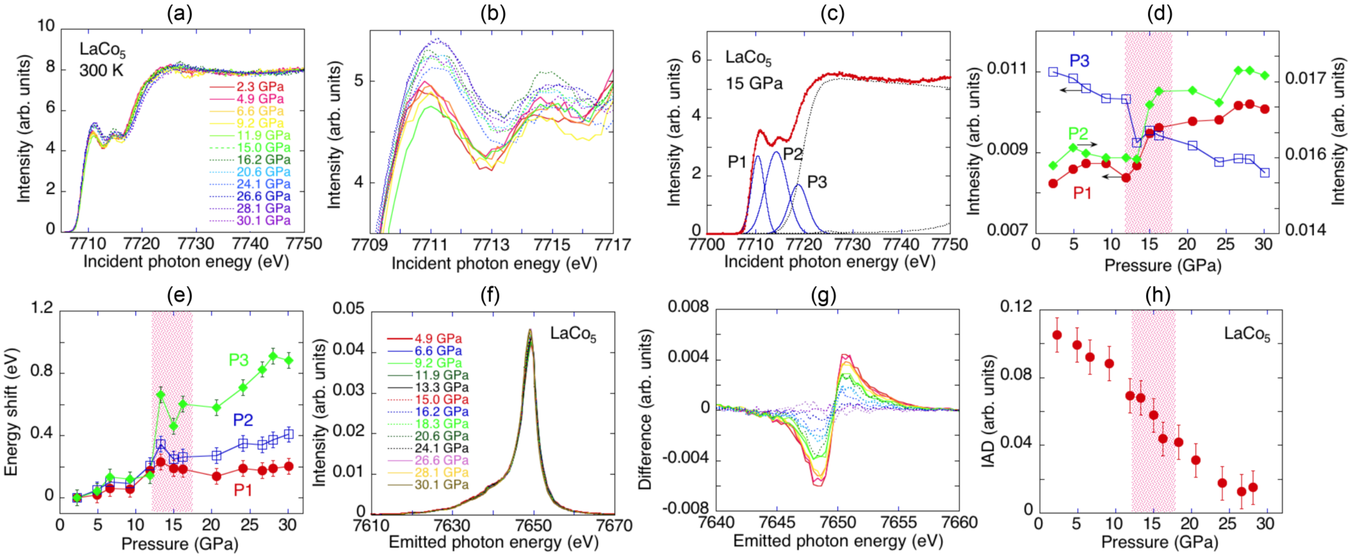

FIG. 2. (a) Pressure dependence of the PFY-XAS spectra. (b) Expanded view of the PFY-XAS spectra around the prepeak. (c) An example of the fit to the PFY-XAS spectrum at 15 GPa. (d) Pressure dependence of the peak intensity in (c). (e) Pressure dependence of the energy shifts of the peaks in (c) relative to the peak energy at 2.3 GPa. (f) Co $K\beta$ x-ray emission spectra. (g) Difference in each XES spectrum at given pressure for a spectrum at 30.1 GPa. (h) IAD values for $LaCo_5$. The shaded areas in (d), (e), and (h) correspond to the pressure range where the lattice constant anomaly was found.

same moments in the high-spin state, while the moment of Co at the 3g site is much smaller than that of Co at the 2c site in the low-spin state after the phase transition [5]. The IAD values are strongly correlated to the local magnetic moment [20,21]. Our results indicate a transition from higher-spin to lower-spin states, a decrease of the magnetic moment with pressure, which is consistent with the band calculations described below.

The LSDA band calculations of YCo_5 indicated that the pressure leads to the broadening of the bands and the shift of the majority-spin Co 3d sharp band edge toward the Fermi level [5,6]. The band edge eventually crosses the Fermi level, and the system becomes unstable, resulting in the decrease of the magnetic moment. A sharp peak near the Fermi level was observed in the valence band photoelectron spectra at ambient pressure for both $LaCo_5$ and YCo_5 [22]. When the sharp edge of the DOS crosses the Fermi level with pressure, the majority and minority DOS have similar high intensity, inducing the thermodynamical instability. The band calculations also showed that the total energy has two minima, corresponding to high-spin and low-spin states. Both states coexist at the transition pressure, and the minimum of the high-spin state disappears at lower volumes, making the high-spin state unstable [5]. It was indicated that the magnetocrystalline anisotropy (MA) energy was enhanced at the transition pressure [9]. The lanthanide contraction in the RCo$_5$ series showed the largest MA energy in $LaCo_5$ and smallest in YCo_5. This indicates that the Lifshitz transition in $LaCo_5$ should be shifted to higher pressures compared to that in YCo_5.

In Fig. 3(a) we compare the band structure of $LaCo_5$ and YCo_5 at 0.4 GPa (near ambient pressure) and 3.1 GPa, respectively. The latter lattice constants have been taken from Rosner *et al.* [6]. Based on the findings of Rosner *et al.* [6], we know that the magnetic collapse from high to low spin state of YCo_5 coincides with the transition of a sharp peak in the occupied majority density of states across the Fermi level. This peak is visible in both calculations (blue and red arrows). However the peak in $LaCo_5$ is located at around 0.2 eV higher binding energies. This suggests a higher transition pressure for La compared to Y.

To qualitatively analyze the evolution of the magnetic state, we calculate the total magnetic moment inside the unit cell of $LaCo_5$ using experimental lattice parameters (closed circles) as well as linearly extrapolated lattice constants to extend the pressure range (open circles). Figure 3(b) shows the presence of a magnetic anomaly around 12–18 GPa. The inset shows the magnetic moment for the expanded pressure range including extrapolated lattice constants. The transition from high to low spin state is predicted to set in around 31 GPa with a steep

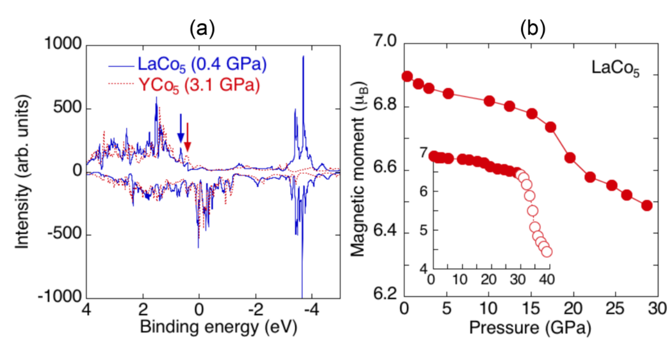

FIG. 3. (a) Density of states for $LaCo_5$ (0.4 GPa) and YCo_5 (3.1 GPa) based on experimental lattice parameters. Main difference is provided by the f-derived unoccupied states around -3 eV to -4 eV binding energies. (b) Calculated magnetic moment inside the unit cell of $LaCo_5$ based on experimental lattice parameters. An anomaly in the evolution of the magnetic moment around 12–18 GPa is visible. The inset shows the magnetic moment for a wider pressure range added via linear extrapolation of experimental lattice parameters. A collapse of the high spin state is predicted for higher pressures.

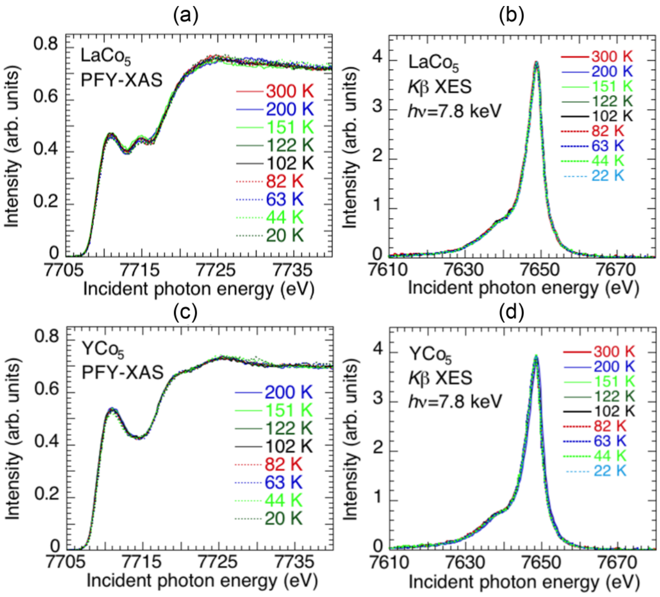

FIG. 4. Temperature dependence of (a) PFY-XAS spectra and (b) $K\beta$ x-ray emission spectra for $LaCo_5$ and (c) PFY-XAS spectra and (d) $K\beta$ x-ray emission spectra for YCo_5.

decrease of the magnetic moment by almost 1.5 μ_B while increasing the pressure to 34 GPa, followed by a less steep reduction towards even higher pressures. Our findings warrant further analysis of the evolution of the electronic band structure around the 12–18 GPa anomaly as well as both theoretical and experimental investigations regarding the predicted presence of the magnetic collapse and a possible Lifshitz transition at pressures higher than 30 GPa.

We also measured the temperature dependence of the PFY-XAS spectra and the $K\beta$ XES spectra of $LaCo_5$ and YCo_5 down to 20 K. No temperature dependence was observed as shown in Fig. 4. Furthermore, our high-resolution valence band spectra near the Fermi level of YCo_5 showed no temperature dependence between 11 and 160 K [22].

The PFY-XAS spectra of YCo_5 in Fig. 4(c) do not show the same double prepeak structure. The spin-resolved density of states of both compounds in Fig. 3(a) exhibits a pronounced difference in the unoccupied states at binding energies from -3 eV to -4 eV where the La-f states are localized in the conduction band of $LaCo_5$. We assume, therefore, the 7715-eV peak in $LaCo_5$ is derived from the Co p states hybridized with the La $4f$ states.

In conclusion, we have measured pressure-induced changes in both electronic and crystal structures in $LaCo_5$. The pressure-induced change in the PFY-XAS spectra and the IAD values suggest the electronic structural transition at the pressure range where the lattice constant ratio of a/c shows an anomalous trend. Thus a transition to lower-spin state, decrease of the magnetic moment, and increase of the hybridization should simultaneously occur. The DFT results suggest that the anomaly in the lattice structure is mutually related to the anomaly in the magnetic moment of the unit cell. DFT further predicts the presence of a magnetic transition similar to YCo_5 at pressures above 30 GPa in $LaCo_5$. The PFY-XAS and Co $K\beta$ XES spectra showed no temperature dependence on the electronic structure at 20–300 K. The difference between the transition pressures between $LaCo_5$ and YCo_5 should be attributed to the different electronic structure near the Fermi level. This is due to the binding energy shift of the flat band near E_F between La and Y, which is key to the Lifshitz transition in RCo_5.

The experiments were performed at SPring-8 Taiwan beamlines BL12XU and BL12B2 (under SPring-8 Proposal Nos. 2014A4136, 2014B4132, 2014B4261, and 2014B4269 corresponding NSRRC Proposal No. 2014-1-053 and 2014-3-053) and at HiSOR BL-9A (Proposal No. 13-A-2) in Hiroshima University. We thank the N-BARD, Hiroshima University for supplying the liquid helium. N.T. and H.Y. have been supported by Grant-in-Aid from JSPS, Nos. 15K05190 and 15K05194, respectively. J.F.L. acknowledges support from HPSTAR.

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[22] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevB.94.165156, which includes Refs. [23–26]. Details of the DFT calculations for $LaCo_5$ and YCo_5, results of RXES, valence band photoelectron spectra at $h\nu = 30$ eV for $LaCo_5$ and YCo_5, and temperature dependence of high-resolution valence band spectra near the Fermi level of YCo_5 at $h\nu = 8.4$ eV are shown.

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