Discovery of paramagnetism with anomalously large magnetic susceptibility in high-pressure phase β(fcc)-cobalt

Pressure-induced magnetic transitions have received much attention because a new phase at high pressure gives considerable insight into the correlation between the crystal structure and ferromagnetism. In 2000, Yoo *et al.* discovered the ε→β (hcp→fcc) martensitic structural transition of Co at ~100 GPa by means of X-ray powder diffraction [1]. Because this transition is regarded to be analogous to the pressure-induced martensitic transition of Fe (ferromagnetic bcc→nonmagnetic hcp at ~14 GPa), they proposed that β-Co is nonmagnetic. Theoretical calculations have also predicted that β-Co is nonmagnetic [2]. However, the transition pressure is so high that the direct observation of the magnetic states has so far not been achieved.

X-ray magnetic circular dichroism (XMCD) is a spectroscopic technique that enables us to probe magnetically polarized electronic states even under high pressure. To investigate the magnetic state of β-Co, XMCD measurement at the Co *K*-edge was carried out at beamline **BL39XU** using a diamond anvil cell. XMCD spectra were measured by the helicity-modulation method. A magnetic field *H* of 0.6 T was applied parallel to the incident X-ray beam and in the direction of surface normal of the sample. In this study, we succeeded in the direct observation of the magnetic state up to 170 GPa [3]. The measurement was done at room temperature. The incident X-ray beam was focused using Kirkpatrick and Baez (K-B) mirrors; a circularly polarized beam with a size of 7 (v) × 6 (h) μm^2 was realized at the sample position, which is a suitable condition for a very small sample in the diamond anvil cell at $P > 100$ GPa.

Figure 1 shows the pressure dependence of XANES spectra. The marked changes in the XANES profile can be recognized in the absorption maximum referred to as **b** (**b**') and **c** (**c**'), which is caused by the ε-β structural transition. The pressure variation in the XANES can be divided into three regions, I, II, and III. The ε-Co single phase is stable in region I, the ε- and β-Co phases coexist in region II, and the β single phase is formed in region III. The boundary pressures were determined to be P_t = 81(8) GPa and P_t' = 134(6) GPa. P_t represents the onset of the structural transition. In region III ($P > P_t'$), the residual ε phase disappears, and Co completely transforms to the β-phase.

The magnetic states in ε- and β-Co are investigated by the pressure variation in the XMCD spectrum shown in Fig. 2. As the pressure increases, the *K*-edge XMCD amplitude shows a gradual reduction. Figure 2 demonstrates that the small amplitude is maintained up to 170 GPa without changes in the spectral shape. The integrated intensity of XMCD, I_{XMCD}, plotted in the inset of Fig. 2, shows that a sharp drop of I_{XMCD} occurs at the onset of the ε-β transition (P_t). As the pressure increases, I_{XMCD} gradually decreases again at region II, and it reaches a constant value at region III above P_t'. The nonzero I_{XMCD} in region III suggests that β-Co possesses finite magnetization due to the magnetic polarization of 3*d* electrons. Hence, β-Co is not nonmagnetic, in contrast to the theoretical predictions.

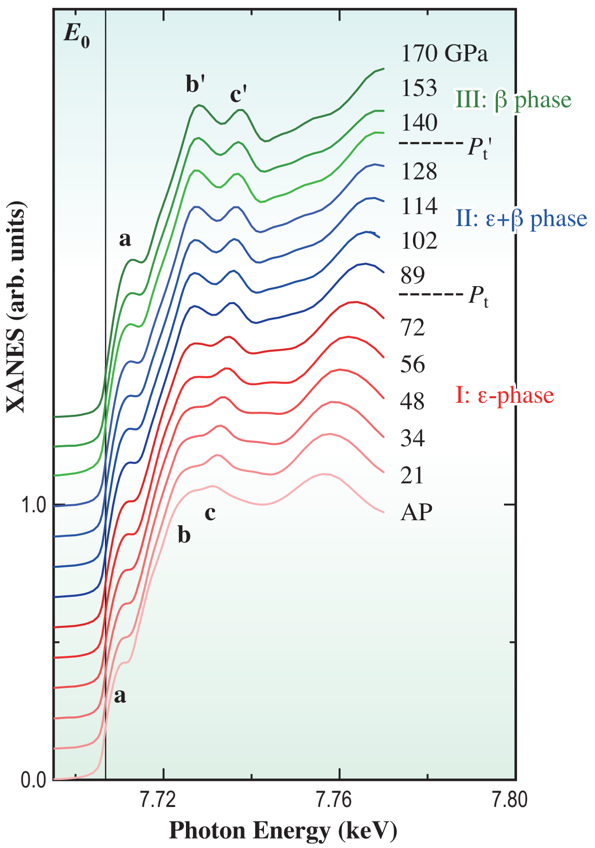

Fig. 1. XANES profiles at the *K*-edge of Co up to 170 GPa. For clarity, each profile is shifted upward. The pressure dependence is divided into three regions, I, II, and III.

In region III, the XMCD amplitude is nearly proportional to the magnetic field (H) and approaches zero at H = 0 T without hysteresis, suggesting that β-Co is paramagnetic. The marked H dependence indicates that measurable magnetization is easily induced by an external magnetic field in the paramagnetic β-Co. Under the assumption that I_{XMCD} is proportional to the magnetization, the mass susceptibility of β-Co is estimated to be $\chi = 1.5(4)\times10^{-3}$ cm^3/g. The evaluated χ is three orders of magnitude larger than the typical value for nonmagnetic 4d and 5d transition metals and is nearly the same as the reported value of γ(fcc)-Co above T_C at ambient pressure (AP). The anomalously large susceptibility indicates that the total energies of the states with and without a finite magnetic moment are comparable. Our result also reveals that the magnetic states of the high-pressure phases in Co and Fe are clearly different. In the case of ε(hcp)-Fe, the zero intensity of XMCD demonstrates the nonmagnetic state of ε(hcp)-Fe [4]. Because this experiment was carried out at room temperature, the magnetic ground state of β-Co is still an open question. There are two possible magnetic states of β-Co: (i) a ferromagnetic ground state with the Curie temperature T_C located below room temperature or (ii) a paramagnetic ground state accompanied with large magnetic susceptibility. The present results encourage theoretical researchers to reexamine the magnetic states of β-Co. XMCD measurements at low temperature should be carried out to investigate the magnetic ground state.

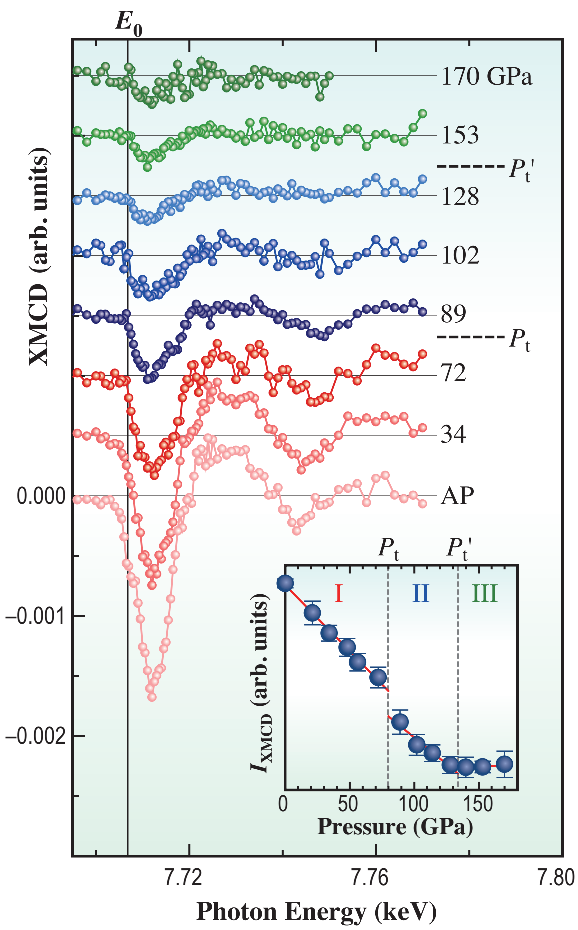

Fig. 2. XMCD spectra at the K-edge of Co at selected pressures. The inset shows integrated intensity of XMCD, I_{XMCD}, as a function of pressure (filled circles).

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