Equation of state of cobalt up to 79 GPa

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(Received 26 January 1996; revised manuscript received 27 March 1996)

Angle-dispersive synchrotron-radiation x-ray powder-diffraction experiments on cobalt were performed by using a diamond-anvil cell and an imaging plate. The hcp phase remained stable up to the highest pressure of 79 GPa. The bulk modulus and its pressure derivative are determined as $B_0 = 199 \pm 6$ GPa and $B'_0 = 3.6 \pm 0.2$, respectively. The axial ratio c/a continuously decreases under pressure. [S0163-1829(96)10326-X]

Cobalt metal has two solid phases. The hexagonal close-packed (hcp) α phase is stable at room temperature and ambient pressure. The face-centered-cubic (fcc) β phase exists at high temperatures above 420 °C, and can be quenched at room temperature as a metastable phase. High-pressure studies on Co are rare. Kennedy and Newton determined the pressure-temperature phase diagram up to 5 GPa and 600 °C.[1] Neither the lattice parameters nor unit-cell volumes have been determined under high pressure. Our recent high-pressure x-ray work on the neighboring element Mn showed evidence for the decrease of magnetic moments under pressure.[2] The disappearance of magnetism may be responsible for the structural transition to a new ε phase at 165 GPa.[2] In the case of Co, we also expect the decrease of the magnetic moment under pressure. Actually for the case of fcc Co, Marcus and Moruzzi predicted a ferromagnetic (FM) to nonmagnetic (NM) transition at 42 GPa with the local-spin-density calculation.[3] Kouvel and Hartelius measured the saturation magnetization of hcp Co under pressure up to about 0.5 GPa at room temperature.[4] They reported a negative pressure dependence of the saturation magnetization, which can be related to the decrease of the magnetic moment under pressure. Accordingly, it is interesting to investigate the crystal structure of Co under high pressure, where the FM to NM transition is predicted. In the present study we report on the phase stability, the equation of state (EOS), and the lattice parameters of Co under high pressure.

Angle-dispersive synchrotron-radiation (SR) x-ray powder-diffraction experiments were performed with a diamond-anvil cell and an imaging plate on the bending magnetic beamline BL-6B at the Photon Factory, National Laboratory for High Energy Physics (KEK). The SR beams were monochromatized to the wavelength 0.6888 Å (18.00 keV) with a sagittally focused Si(111) double monochromator. We used two different sample assemblies for low- and high-pressure regions. The former had a pair of diamond anvils with 400 μm culets, a gasket with 150 μm ϕ hole and 80 μm thickness, and was utilized for a pressure range up to 47 GPa. The latter had a pair of diamond anvils with 300 μm culets, a gasket with 70 μm ϕ hole and 70 μm thickness, and was used for higher pressures. Udimet 700 (Ni-based alloy) was used as a gasket material. A 4:1 mixture of methanol and ethanol was used as a pressure transmitting medium. The pressures were determined by the ruby fluorescence method.[5] Cobalt powder was obtained from Koch-

Light Laboratories Ltd. (99.5% purity, 1 μm particle size). The powder was found to be fine enough, judging from the smooth Debye-Scherrer rings recorded on an imaging plate. The two-dimensional image was converted to an ordinary one-dimensional diffraction pattern with the method we have already reported.[6] All the experiments were done at room temperature.

Figure 1 displays the powder-diffraction patterns of Co under pressure. The prefixed h and f before the Miller indices represent the hcp and fcc phases, respectively. The starting powder was a mixture of the hcp and fcc phases with fcc as a dominant component. On small compression, the fcc
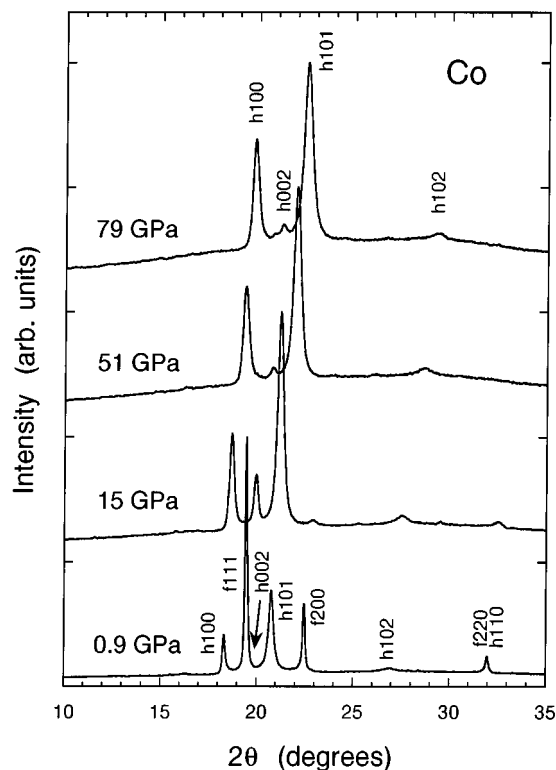

FIG. 1. X-ray powder-diffraction patterns of cobalt under high pressure. The prefixed h and f before the Miller indices represent the hcp and fcc phases, respectively. The fcc phase, which is metastable under ambient conditions, fully transformed to the hcp phase around 24 GPa. No phase transition from the hcp phase was observed.
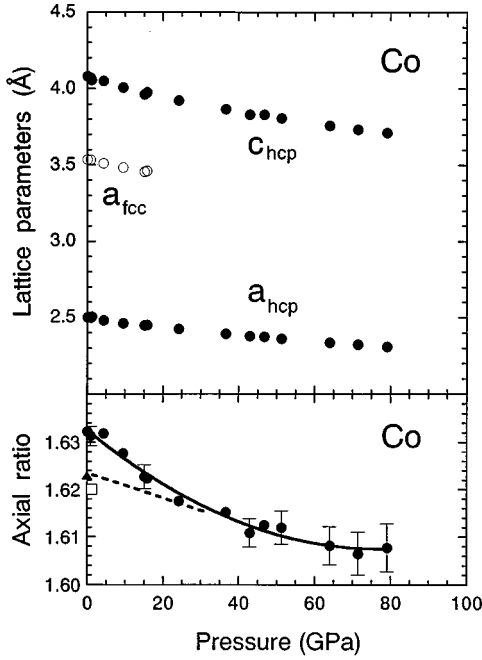
FIG. 2. The pressure dependence of the lattice parameters (top) and the axial ratio c/a (bottom) of cobalt. Open and closed circles in the top panel represent the lattice parameters of the fcc and hcp phases, respectively. In the bottom panel, the open square means the down-loaded point from 79 to 1.2 GPa. The closed triangle shows the axial ratio at ambient pressure from literature. The solid curve shows the fit to the circles with a second-order polynomial. The dashed curve shows the pressure dependence of the axial ratio expected for the pure hcp phase.

phase gradually transformed to the stable hcp phase, and completely disappeared above 24 GPa. Since the phase boundary between the hcp and fcc phases has a positive slope dT/dP in the pressure-temperature phase diagram,[1] the hcp phase should become more stable at room temperature with increasing pressure. No phase transition from the hcp phase was observed up to 79 GPa.

The lattice parameters of the fcc and hcp phases are plotted as a function of pressure in Fig. 2 (top), which were calculated by the following procedure. The peak positions of $h100$, $f111$, $h101$, and $f200$ were determined by deconvoluting them with a profile fitting program. The peak position of $h102$ was fitted as an independent peak. The peak of $h002$ was ignored because of its weak intensity due to the preferred orientation and overlapping with $f111$. The lattice parameter for the fcc phase (a_{fcc}) was determined from the peak position of $f200$ to avoid the effect of overlapping of $f111$ with $h002$. The lattice parameters for the hcp phase (a_{hcp} and c_{hcp}) were determined from the peak positions of $h100$, $h101$, and $h102$ for the same reason.

Figure 2 (bottom) represents the pressure dependence of the axial ratio c/a of the hcp phase. The axial ratio continuously decreases under pressure. The data are fitted with a second-order polynomial as shown with the solid curve. The axial ratio at ambient pressure was 1.632 ± 0.002 in our experiment. This value is significantly larger than the value found in literature (1.623), which is shown with a closed triangle. The difference can possibly be explained by the effect of coexistence of the hcp and fcc phases: The starting
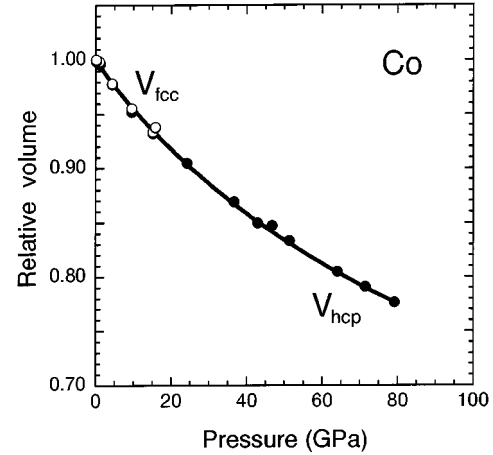

FIG. 3. The relative volumes of fcc (V_{fcc}, open circles) and hcp (V_{hcp}, closed circles) normalized to the hcp volume at ambient pressure. V_{fcc} is found to be 0.2% larger than V_{hcp} at any pressures. Solid curve represents the fitted Vinet EOS for the hcp phase.

powder used in Fig. 1 is almost fcc at ambient pressure. If an hcp domain is surrounded by fcc domains, the hcp domain may be deformed to match the fcc stacking having the ideal axial ratio of 1.633. To confirm this hypothesis, we measured the axial ratio for the hcp single phase at ambient pressure. The hcp single phase was obtained by grinding the starting powder (a mixture of fcc and hcp) for 30 min. The sample thus prepared gave the axial ratio of 1.623, same as literature. The hcp single phase was also obtained, when the starting powder was pressurized to high pressures and then recovered to low pressures. The open square in Fig. 2 (bottom) represents the axial ratio for the sample recovered from 79 to 1.2 GPa. The axial ratio of 1.620 ± 0.002 is in reasonable agreement with the literature value of 1.623 at ambient pressure. We guess therefore that the pressure dependence of the axial ratio for the pure hcp phase should be drawn as the dashed curve in Fig. 2 (bottom).

Figure 3 shows the relative volumes of the fcc (open circles V_{fcc}) and hcp (closed circles V_{hcp}) phases normalized to the hcp volume at ambient pressure. The volume of the fcc phase was found to be always 0.2% larger than that of the hcp phase in the pressure range up to 16 GPa. By fitting the data for the hcp phase with the Vinet EOS,[7] we obtain the bulk modulus and its pressure derivative as $B_0^{hcp} = 199 \pm 6$ GPa and $B_0' = 3.6 \pm 0.2$, respectively. The bulk modulus is close to the result of an ultrasonic experiment $B_0 = 190$ GPa.[8] For the fcc phase, we obtain the same bulk modulus $B_0^{fcc} = 199$ GPa as B_0^{hcp}.

Söderlind et al. calculated the bulk modulus for FM fcc Co as $B_0 = 195.5$ GPa with the full potential linear muffin-tin orbital (FP-LMTO) method.[9] This value is very close to the present experimental value of $B_0^{fcc} = 199$ GPa. There are few theoretical calculations of the bulk modulus for hcp Co. Jarlborg and Peter calculated the band structure of Co by the LMTO method, and obtained the value of $B_0 = 220$ GPa for both the FM fcc and hcp structures.[10] There seems to be very little difference between the fcc and the hcp bulk moduli as confirmed by the present experiments.

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