Anomalous pressure evolution of the axial ratio *c/a* in hcp cobalt: Interplay between structure, magnetism, and lattice dynamics

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We performed angle-dispersive x-ray diffraction measurements on hydrostatically compressed hcp cobalt to 90 GPa. Near 75 GPa, we document an inversion in the pressure derivative of the axial ratio c/a with no discontinuity in the volume and lattice parameters compression curves. These results are also reproduced by *ab initio* calculations. Our study indicates significant interactions among structure, magnetism and elasticity, suggesting that the collapse of the magnetic moment is responsible for the observed anomaly in c/a, as well as for the anomalies in the elastic and vibrational properties of hcp Co at high pressure. © *2008 American Institute of Physics*.
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The structure and elastic properties of 3*d* transition metals strongly depend on the *d*-electron occupancy and their magnetic state.[1] At ambient conditions, progressive filling of the 3*d* bands drives the stable elemental phase from bcc (iron), to hcp (cobalt), and finally fcc (nickel). Increasing pressure also stabilizes the hcp and then the fcc structure over the bcc structure. In both cases, suppression of the magnetic moment is considered the driving parameter. Indeed, compression typically leads to a broadening of the electronic bands and hence to a reduction of the density of states at the Fermi level, eventually driving the system to a nonmagnetic state.

Among all the elements or ordered compounds, cobalt exhibits a nonzero magnetic moment over the largest *P-T* domain. At ambient pressure Co is ferromagnetic, and its stable structure is hcp. At high temperature (695 K), Co undergoes a phase transition from the hcp to the fcc structure, retaining a magnetic moment up to 1400 K.[2] At ambient temperature the hcp phase is stable up to 100 GPa, where it transforms martensitically to a fcc phase in the 105–150 GPa range.[3] In contrast to the high-temperature phase, the Co high-pressure fcc phase is suggested to be nonmagnetic.[2–5]

Well below the high-pressure hcp-fcc transition, the elastic and vibrational properties of cobalt display anomalous behavior:[5–7] the aggregate sound velocities show a departure from the linear evolution with density, with a decrease in the E_{2g} mode Grüneisen parameter.[6,7] While it is clear that there are strong elastic anomalies in the 70–80 GPa pressure range, quite surprisingly, there has been no indication of any structural discontinuity. Two independent experimental studies[3,8] report a compression curve that is well described by a single third order Birch–Murnaghan equation of state (EOS), with bulk modulus K_0 and its pressure derivative K', equal to 199 ± 6 GPa and 3.6 ± 0.2, respectively. However, the cobalt sample was not hydrostatically compressed in either of the two experiments, and neither study was able to map with sufficient precision the pressure evolution of the axial c/a ratio.

Therefore, we have undertaken an x-ray powder diffraction study on pure hcp cobalt, nearly hydrostatically compressed in neon pressure medium. Our goal was to accurately document the pressure evolution of the c/a ratio and to highlight any possible effect linked to the anomalies in the elastic properties. We have complemented our experiments with all electron first principles computations, which closely track the c/a ratio with compression for both ferromagnetic and nonmagnetic hcp cobalts.

Experimentally, the presence of naturally occurring metastable fcc cobalt is a significant hindrance to accurate fitting of diffraction patterns.[8] Based on our previous experience with uniaxially compressed polycrystalline cobalt,[9] we have obtained pure hcp samples by compressing 99.999% purity cobalt powder to 5 GPa into a diamond anvil cell (DAC) with no pressure medium, and then quenching in liquid nitrogen. The recovered powder was then loaded, together with platinum powder and a ruby sphere as pressure calibrants, into rhenium gasket using neon as pressure transmitting medium. We employed two membrane type DACs, both equipped with beveled diamond anvils (150 μm flat beveled from 300 μm culet at 8°).

We performed angle-dispersive x-ray diffraction measurements at the ID09A beamline of the ESRF (Grenoble, France), using a monochromatic beam ($\lambda = 0.4121$ Å) focused down to less than 15×15 μm^2 full width at half maximum. More than 50 diffraction patterns were collected at room temperature in the 0–90 GPa pressure range, throughout the entire stability field of the hcp phase. Particular care was taken to stabilize the pressure and to minimize the drift during the measurements. Pressure was measured by ruby luminescence[10] before and after each collection of the Co diffraction, and confirmed by x-ray diffraction of the Pt in-

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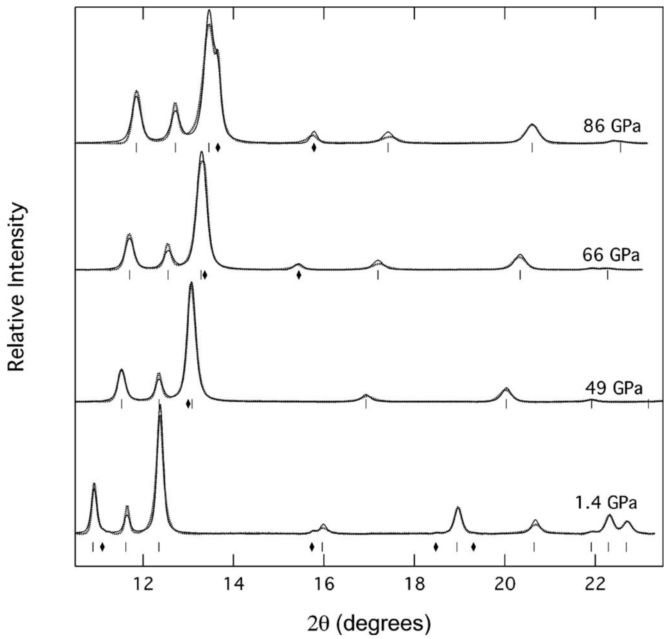

FIG. 1. Integrated diffraction patterns of hcp cobalt at high pressure (dots: experimental data; solid line: equally weighted structural refinement). Six to nine reflections from hcp Co, highlighted by thick marks, are resolved in each pattern. Ne reflections are indicated by diamonds.

ternal standard.[11] Figure 1 shows representative high-pressure diffraction patterns of cobalt.

Our hcp-Co diffraction patterns have no evidence of contamination from the fcc phase, nor from the pressure markers or the gasket at any pressure. Analysis of the individual *d* spacings and pressure-induced broadening of the Co and Pt diffraction lines provides evidence of an overall good hydrostaticity over the entire investigated pressure range. The compression curve is reported in Fig. 2, together with the weighted third-order Birch–Murnaghan fit to the experimental data, which yields $K_0=203\pm2$ GPa and

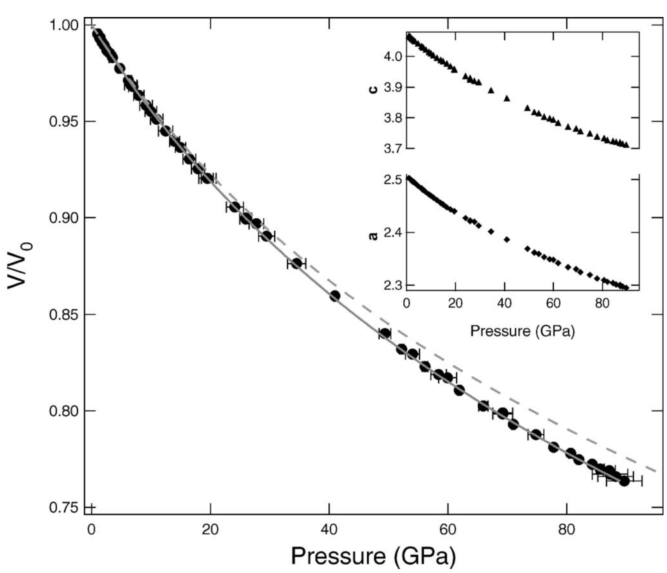

FIG. 2. Isothermal compression curve of hcp Co at ambient temperature. The uncertainties on volume and relative pressure are smaller than the symbols; the error bar on the absolute pressures reproduce the difference between the ruby-luminescence pressure (Ref. 10) and the Pt-EOS pressure (Ref. 11). The solid line is a third-order Birch–Murnaghan fit to the experimental data; the dashed line is the computed compression curve. Inset: pressure evolution of the lattice parameters (values in angstroms).

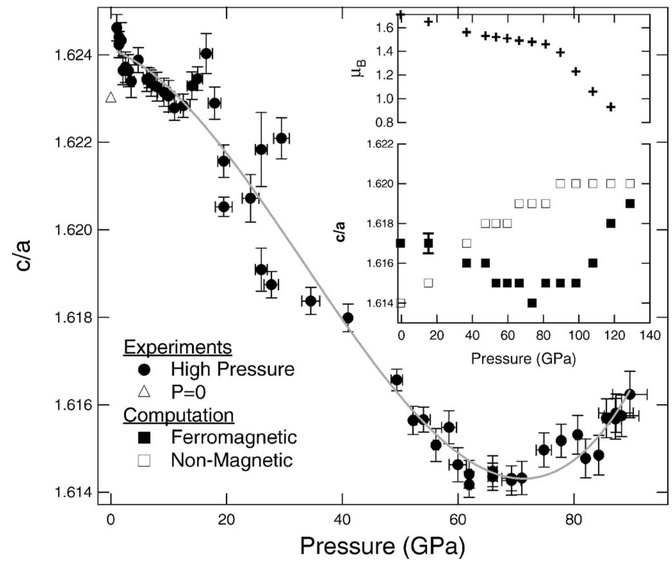

FIG. 3. Pressure evolution of the axial ratio. The solid line is a polynomial fit to the experimental data. Literature data (Refs. 3 and 8) have a variance that does not allow them to be plotted at this scale. Inset: theoretically predicted pressure evolution of the magnetic moment and computed values of c/a.

$K'=3.6\pm0.1$, in good agreement with previous determinations.[12] However, we observe a markedly different behavior in c/a from that of previous experimental work on foils[3] and *ab initio* calculations.[5,13] Our data display a monotonic decrease in the axial ratio with a minimum ~70–75 GPa. Above this pressure, c/a has a positive pressure dependence (Fig. 3). While a continuous decrease of the axial ratio with pressure was observed in previous diffraction experiments,[8] the less dense sampling over a less extended pressure range, and the larger error bars, prevented a clear detection of the change in the slope.

Interestingly, the inversion in the pressure evolution of the axial ratio takes place in the same pressure interval where the anomalies in the elastic and vibrational properties have been observed.[6,7] Discontinuities in the pressure evolution of c/a have been experimentally observed or theoretically predicted in other hcp metals [e.g., Zn, Cd, and Os (Refs. 14–18)], often associated with effects on the elastic properties. The link between these phenomenologies and Lifshitz[19] transitions is a matter of extensive debate. YCo_5 also displays an abrupt change in the c/a at ~19 GPa,[20] connected to a volume reduction of about 1.5%, arising from a lattice collapse along the *c* axis. Calculations of the magnetic moment and of the electronic density of states point to a magnetoelastic coupling as the origin of the volume collapse, and the anomaly has been described as a first-order Lifshitz transition.[20] In the case of hcp Co as well, a link between structure and magnetism, through a strong correlation of the axial ratio with the magnetic moment and magnetocrystalline anisotropy, is well established from both experimental and theoretical studies.[21,22] However, despite the conceptual similarity, the present case is different in that there is no measurable volume collapse and the axial compression of both *a* and *c* is smooth and regular (Fig. 2).

To shed light on the origin of the axial ratio anomaly and on the potential link with the elastic and vibrational properties, we performed full-potential linearized augmented plane-wave[23] calculations, implemented in the WIEN2K code,[24,25] using the generalized gradient approximation to the exchange-correlation potential.[26] We carried out computations for volumes of 52–75 $bohr^3$ (pressure of 0–140 GPa) with a dense volume sampling (ΔV=1 $bohr^3$ for V =52–63 $bohr^3$). We kept the muffin tin radius R_{MT}=2.0 constant over the whole compression range. Total energies were evaluated for c/a ratios between 1.55 and 1.69, in steps of 0.01. The equilibrium c/a was obtained from fitting a quadratic polynomial in (c/a-1.61) to the $E-c/a$ curve at constant volume. Reciprocal space was sampled on a $16\times16\times8$ k-point mesh, and $R_{MT}K_{max}$=9.0 was used.

The computed equilibrium values for the axial ratio are reported in the inset of Fig. 3. In spite of a slight offset in the absolute values at low compression, the spin-polarized calculations compare favorably with the measurements.[27] Most importantly, the c/a ratio of ferromagnetic hcp cobalt decreases with pressure until ~75 GPa (59 $bohr^3$) and then increases, progressively approaching the values computed for the nonmagnetic phase, which, conversely, monotonically increases over the entire pressure range. A comparison with the pressure evolution of the magnetic moment (inset Fig. 3) provides the most direct explanation for the observed behavior: compression induces a slow reduction of the magnetic moment up to 70–80 GPa, above which the magnetism is rapidly lost and the axial ratio c/a of ferromagnetic cobalt changes its pressure derivative, coming up to match the c/a values of nonmagnetic cobalt. This scenario is also supported by the linear decrease of the magnetization energy with compression, which reaches zero near 130 GPa (53 $bohr^3$). This magnetoelastic coupling likely also drives a softening of the elastic moduli and provides an explanation for the deviation from a linear density dependence seen in the aggregate sound velocities.[6,7]

While the proposed model is consistent with previous experimental[2,3,6,7] and computational work,[5,13] recent x-ray magnetic circular dichroism measurements[4] report a rapid and uniform decrease of the magnetic dichroism with compression, suggesting a constant decline in magnetic moment over the entire hcp phase stability range. These results differ from the predictions of density functional theory,[5,13] and measurements of the pressure dependence of the Curie temperature.[2,28] Indeed, the Curie temperature, which is proportional to the product of magnetic moment and magnetic exchange, slightly increases with pressure at least up to 25 GPa. Thus, it is highly unlikely that the magnetic moment decreases by a significant amount up to this pressure. Resolving these issues will critically hinge on future confirmation of the x-ray magnetic circular dichroism measurements.[4]

In conclusion, we have shown an inversion in the pressure derivative of the axial c/a ratio in hcp Co around 75 GPa, which correlates with previously recognized anomalies in the elastic and vibrational properties. A comparison between our spin-polarized and nonmagnetic calculations and the experimental results provides strong evidence for significant interactions among structure, elasticity, and magnetism. We argue that, due to strong magnetoelastic coupling, the compression-induced loss of the magnetic moment above 75 GPa is responsible for the inversion in the pressure derivative of the axial ratio as well as of the softening of the aggregate velocities.

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