# Magneto-elastic lattice collapse in $YCo_5$

H. Rosner,[1*] D. Koudela,[2] U. Schwarz,[1] A. Handstein,[2] M. Hanfland,[3] I. Opahle,[2] K. Koepernik,[2] M. Kuz'min,[2] K.-H. Müller,[2] J. Mydosh,[1] M. Richter[2]

[1]Max-Planck-Institut für Chemische Physik fester Stoffe,
Nöthnitzer Straße 40, 01187 Dresden, Germany
[2]IFW Dresden,
P.O. Box 270116, 01171 Dresden, Germany
[3]ESRF, BP220, 38043 Grenoble, France

[*]To whom correspondence should be addressed; E-mail: rosner@cpfs.mpg.de.

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**Abstract**

Isomorphic lattice collapse of crystalline lattices under pressure is a rare and intriguing phenomenon, the most famous examples being samarium sulfide and cerium metal. They are cubic under ambient conditions and collapse isomorphically under pressure, with about 15% volume reduction.[1, 2, 3] In SmS the transition is ascribed to a change of the $4f$ chemical valence. The collapse in Ce is connected with altering contributions of the $4f$-electrons to the chemical bonding, though details are still debated.[4, 5] In contrast, the investigated $YCo_5$ is a compound with a stable valence and without $4f$ electrons. We have found that an entirely new type of isomorphic transition occurs in this hexagonal metallic compound under hydrostatic pressure of 19 GPa. Here, the lattice collapse is driven by magnetic interactions and can be characterized as a first-order Lifshitz transition. This is shown in a combined investigation using ab-initio electronic structure calculation and high-pressure x-ray diffraction. Our studies prove the existence of a bistable bonding state due to magnetoelastic interaction.

Since centuries, phase transitions in solids play a key role in tailoring material properties, e.g., in steel-technology. More recently, scientists have been intrigued by isomorphic phase transitions under pressure, where a dramatic change of the electronic structure triggers a vol-

ume collapse, while the atomic arrangement in the structure is preserved. Such transitions provide a unique opportunity for studying the fundamentals of chemical bonding. In general, high pressure is the most appropriate tool to study the effect of modified atomic distances on physical, chemical, and material properties. Alternatively, similar modifications can be achieved by substituting chemically similar elements with different atomic radii. In contrast to the chemical substitution, high pressure has the advantage that the chemical bonding can be modified without changing the composition. Specifically, chemical substitution introduces disorder and local strain in the atomic lattice, while external pressure preserves the lattice homogeneity. Recent progress in high-pressure technology now makes it possible to study materials under hydrostatic compression even at low temperatures up to the megabar region – that is several million times the atmospheric pressure and comparable to pressures in the earth's core. In particular, itinerant magnetism of transition metals is sensitive to pressure. Iron, the prototype ferromagnetic element and main constituent of the earth's core, becomes non- magnetic under a transition pressure of about 65 GPa (0.65 Mbar).[6]

Among all known elements and ordered compounds, cobalt metal exhibits the most stable magnetic behaviour, indicated by its magnetic ordering temperature $T_C$ of almost 1400 Kelvin, higher than that of any other element or compound. Even under the extreme pressure of 120 GPa the Co magnetism is only partially suppressed.[7] If diluted with moderate amounts of nonmagnetic metals, Co largely retains its strong magnetic properties. The Co-rich intermetallic compounds $Y_2Co_{17}$ (90% Co, $T_C \approx 1200$ K) and $YCo_5$ (83% Co, $T_C \approx 1000$ K) are strong ferromagnets with completely filled majority spin states in the Co-3$d$ band. This means that the Co spin moment almost retains its maximum atomic value, only slightly reduced by hybridization. Compounds of such compositions ($SmCo_5$ and $Sm_2Co_{17}$) are frequently used in permanent magnet applications.[8] In contrast, $YCo_2$ (67% Co) shows no spontaneous magnetic order, but becomes ferromagnetic when a strong magnetic field of 69 Tesla is applied.[9]klops

These facts select $YCo_5$ as a most suitable compound for high pressure studies: It still has a high ordering temperature but is expected to show a much stronger sensitivity to pressure than Co metal. Earlier theoretical studies [10] suggested the existence of a low-moment phase of $YCo_5$ at a volume close to 90% of that at ambient conditions. This phase has never been observed. The isostructural compound $ThCo_5$, on the other hand, exhibits a metamagnetic

transition [11, 12] similar to that in $YCo_2$, indicating that $YCo_5$, too, may be close to a magnetic instability.

First, we have studied the electronic structure of $YCo_5$ by means of the high-precision full-potential local-orbital (FPLO) computational method [13] (see Methods) and found the transition pressure within the experimentally available region. Our results predict a collapse of the lattice connected with a reduction of the magnetic moment by one third. Although the transition is isomorphic, i.e. it preserves the symmetry of both the lattice and the atomic sites (see Figure 1), the sudden change of lattice parameters is predicted to be significantly anisotropic. Whereas the atomic distances in the hexagonal plane are almost unaffected, the inter-plane spacing shrinks considerably.

High-pressure experiments were performed (see Methods) at the European Synchrotron Radiation Facility (ESRF) Grenoble in order to detect the predicted anomaly. The results (see Figure 2) show a remarkable agreement between the theoretical and experimental volume dependence of the lattice parameter ratio, $c/a$.

From the comparison of theoretical and experimental data it is possible to assign the sudden change of $c/a$ at 19 GPa pressure to a magneto-elastic transition. The two segments of the theoretical curve in Figure 2, where $c/a$ grows with increasing pressure (decreasing volume), belong to the high- moment and low-moment phases, while the steep drop at a cell volume of about 74 $Å^3$ belongs to a metastable region. Such a thermodynamically unstable region is characteristic for a first-order phase transition and can be identified by calculating the free enthalpy of the system. Because it is thermodynamically impossible to transfer one phase into the other through a continuous sequence of equilibrium states, the system chooses non- equilibrium paths depending on in- and external parameters, fluctuations and real structure, including the formation of domain patterns. Thus, different paths are taken for increasing and decreasing pressure. This phenomenon, called hysteresis, is a fingerprint of first-order phase transitions. It is clearly observed in the present experiments (see Fig. 2; area between the blue curves in the transition region).

The calculated volume reduction $\Delta V/V = 1.3\%$ agrees well with the experimental value, $\Delta V/V$ $1.6\pm0.9\%$, although the observed anomalies are less sharp due to the finite measurement temperature (T=100 K).

The measured x-ray diffraction patterns show the predicted anomalies of the lattice parameters but no indication of any other structural or symmetry change. Consequently, the transition that $YCo_5$ undergoes at 19 GPa is an isomorphic first-order phase transition. This is the first-ever observation of a pressure-induced isomorphic volume collapse of an itinerant magnet. A few other systems exhibit isomorphic transitions under pressure as well, e.g. cerium [1, 2], samarium sulfide,[3] barium silicide $Ba_8Si_{46}$,[14] and osmium.[15] The physical mechanism of the transition in $Ba_8Si_{46}$ is unknown, and the transition in Os is not of first order. In the first two examples, the number of electrons that contribute to the chemical bonding and the state of the $4f$ electrons change at the transition, thereby yielding a volume collapse of about $15\%$. In the present case, a completely different physical mechanism, the magnetoelastic interaction, causes the collapse. The related volume change of about $1.6\%$ is smaller than in the case of Ce or SmS. This is to be expected since magnetic interactions are weak ($T_C \approx 1000$ K $\approx 0.1$ eV/$k_B$) in relation to the energy 1eV characteristic of the chemical bond.

At ambient conditions, $YCo_5$ is a strong ferromagnet like pure cobalt metal, i.e., its magnetism is only little susceptible to moderate changes of thermodynamic variables. In particular, the magnetic moment is rather stable since the majority-spin Co-$3d$ band is completely filled (Fig. 3, black line). The application of strong pressure reduces the atomic distances and increases the overlap of the valence orbitals. This leads to a broadening of the related bands. As a consequence, the majority Co-$3d$ band edge moves towards the Fermi energy $\varepsilon_F$ (Fig. 3, upper panel, blue line). As soon as the sharp peak crosses the Fermi level, the majority density of states (DOS) and the minority DOS have similarly high values, leading to an instability of the thermodynamic state. Quantitatively, this scenario is described by a generalized Stoner criterion.[16] At the transition pressure the system transforms into a new stable state characterized by a smaller magnetic moment, a smaller volume and a reduced $c/a$ ratio. Microscopically this is achieved by partly depopulating the majority-spin channel. The band edge peak (Fig.3, red line) is now situated well above the Fermi level.

The nature of the magnetoelastic coupling, responsible for the transition, can be understood in the framework of the Friedel model.[17, 18] For the non-magnetic $4d$ transition metal series (Figure 4, black curve) the successive filling of the bonding, non-bonding and anti-bonding states results in a parabolic dependence of the binding energies and therefore the interatomic

distances on the number of valence electrons. In the $4d$ series the magnetic interaction is relatively weak and cannot compete with the elastic energy. In contrast, magnetic order occurs in the second half of the $3d$ series. Here, the related metals show pronounced deviations from the expected parabolic behaviour (Fig. 4, red curve) towards larger distances and weaker bonds driven by a gain in magnetic energy. The magnetic order shifts the majority states to lower energy and, in the case of Co and also $YCo_5$, increases the occupation of the antibonding majority spin states resulting in a loss of bonding energy. The corresponding depopulation of the minority spins has less influence since it moves the nonbonding states to the Fermi level (inset Fig. 4, left panel). In contradistinction, application of high pressure to $YCo_5$ favours the elastic part of the energy balance and reduces the magnetic moment. Accordingly the anti-bonding states are depopulated (inset Fig. 4, right panel), the system gains additional bonding energy and the volume shrinks suddenly. Although the balance between magnetic and elastic energy is a general feature, a first-order collapse is not expected in all magnetic systems. It is related to the specific electronic structure of $YCo_5$ showing a narrow peak close to the Fermi energy (see Fig. 3). This peak originates solely from the Co-$3d_{xz}$ and $3d_{yz}$ orbitals (see Fig. 3, inset). Their bonding increases due to the depopulation of the antibonding states leading to the observed anisotropic lattice collapse.

Already in 1960, Lifshitz predicted that elastic anomalies can occur if the topology of the Fermi surface changes under pressure while preserving the number of valence electrons.[19] As in the case of Os,[15] such electronic topological transitions are in general not of first order. Only when the related singularity in the DOS is exceptionally strong, does the compressibility become negative and the lattice suddenly collapses. If this transition is isomorphic, it is called a first order Lifshitz transition.[19] In the case of $YCo_5$, the topology of the Fermi surface changes (see supplementary information) when the very strong DOS peak gets depopulated (see Fig. 3). This qualifies $YCo_5$ as the first clear example of a first-order Lifshitz transition, related to the existence of a bistable bonding state due to magnetoelastic interaction.

Beyond its fundamental interest,[20] studies of magnetoelastic properties are of major importance for the development of high-tech materials. Magnetic-shape-memory alloys [21, 22] exhibit extraordinary magnetoelastic strains and are candidates for actuator or strain-sensor applications. On the other hand, magnetostriction is undesirable in magnetic refrigerants [23]

where one tries to minimize hysteretic losses.[24]

## Methods

### Experiment

Mixtures of the elements (stated purity: Y 99.9 %, Co 99.95 %) in a molar ratio of 1:5 were arc-melted in purified argon atmosphere. The $YCo_5$ button was homogenized by annealing at 1100°C for 7 days, followed by crushing and milling to a grain size smaller than 20 $\mu$m. To reduce residual mechanical stress in the grains, the powder was annealed at 800°C for 30 min in Ar. X-ray diffraction revealed single phase material. Bulk samples from the same batch were polished and characterized by optical microscopy and wave-length dispersive electron microprobe.

High pressures were generated using a diamond anvil cell equipped with a samarium-doped strontium borate crystal as a pressure sensor [25, 26] and helium as a pressure transmitting medium. Diffraction experiments using synchrotron radiation at ID09 (wave length 41.753 pm) of the ESRF were performed at various pressures up to 33 GPa and temperatures (sample 1 measured at T = 140 K, sample 2 at T = 100 K). Integration of powder rings was realized by means of the computer program Fit2d (see supplementary information).[27] For the determination of peak positions, indexing of diagrams, and lattice parameter refinements the program package WinCSD [28] was used.

### Theory

A full potential non-orthogonal local-orbital (FPLO, release 3.00-5) scheme [13] was employed to obtain highly accurate total energies. In the scalar-relativistic calculations within the local spin density approximation (LSDA) we used the exchange and correlation potential of Perdew and Wang.[29] As the basis set, Co($3s, 3p, 4s, 4p, 3d, 4d$) and Y ($4s, 4p, 4d, 5s, 5p, 5d$) states were chosen. The lower lying states were considered as core states that are treated fully relativistically. A k-mesh of 46656 (36x36x36) points in the Brillouin zone was used. Convergency with respect to basis set and k-mesh was carefully checked to ensure the required relative accuracy of $10^{-12}$ in the total energy. The calculated pressures have been offset-corrected to zero for the experimental unit cell volume.

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## Competing financial interests

The authors declare that they have no competing financial interests.

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# Figures

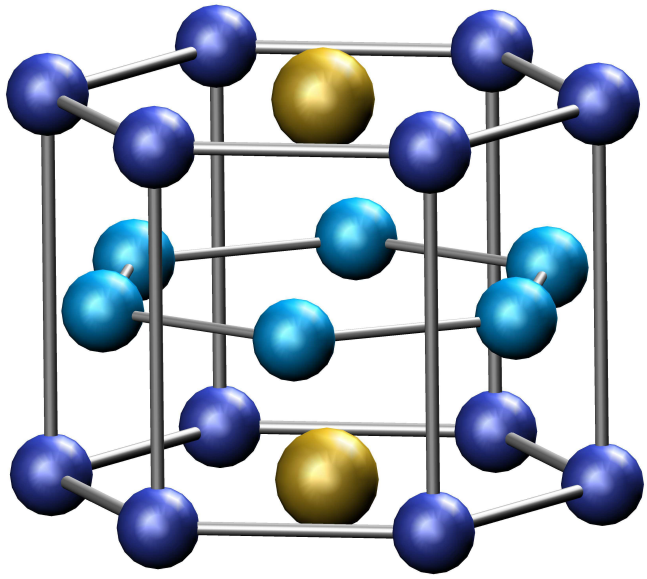

**Fig. 1.** The hexagonal crystal structure of $YCo_5$. Yttrium atoms in the center of the hexagons are presented by golden spheres, the two crystallographically non-equivalent cobalt atoms at the corners and on the prism face centers are illustrated by dark and light blue spheres.

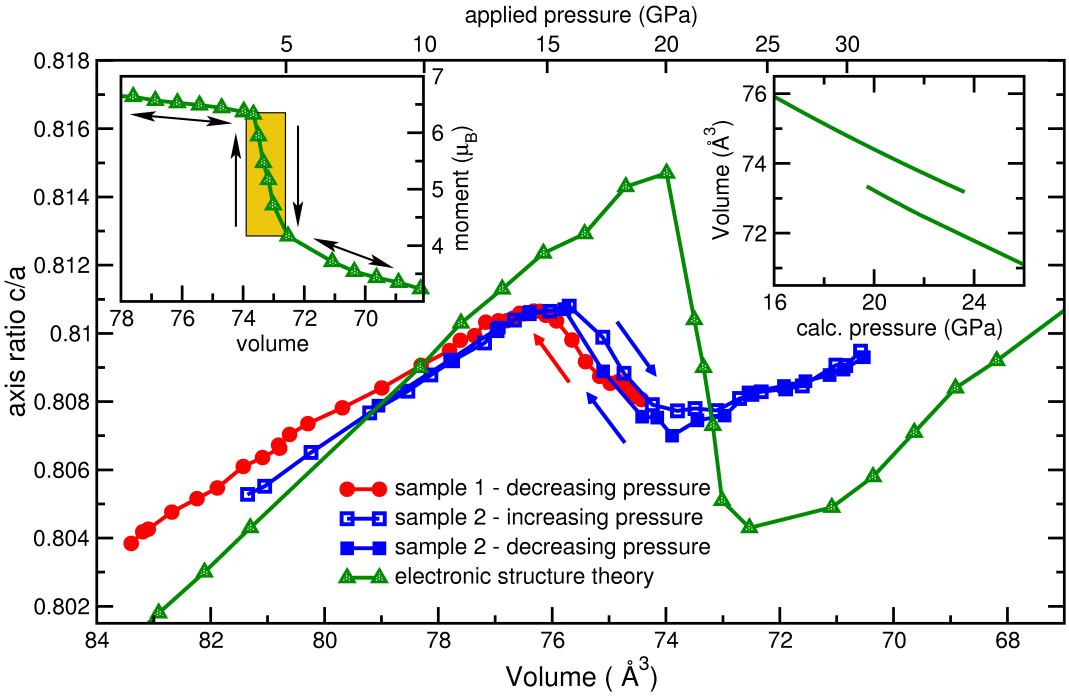


**Fig. 2.** Lattice collapse along the hexagonal c-axis in $YCo_5$ under pressure up to 33 GPa. The blue and the red curves show the measured $c/a$ ratios for two different samples, the green curve is the result of the electronic structure calculations. Applying pressure reduces the volume of the crystal at first continuously, then at 19 GPa a sudden drop of the c-axis and a related volume collapse is observed. The right inset presents the predicted volume collapse of 1.3% calculated from the equation of states of the low- and the high-pressure phase. The left inset shows the concomitant breakdown of the calculated magnetic moment and the thermodynamically unstable region (yellow) as calculated from the free enthalpy. The expected hysteresis caused by this instability is indicated schematically by arrows. This hysteresis is apparent in the experimental data for increasing and decreasing pressure conditions (area between the blue curves with open and full symbols in the transition region).

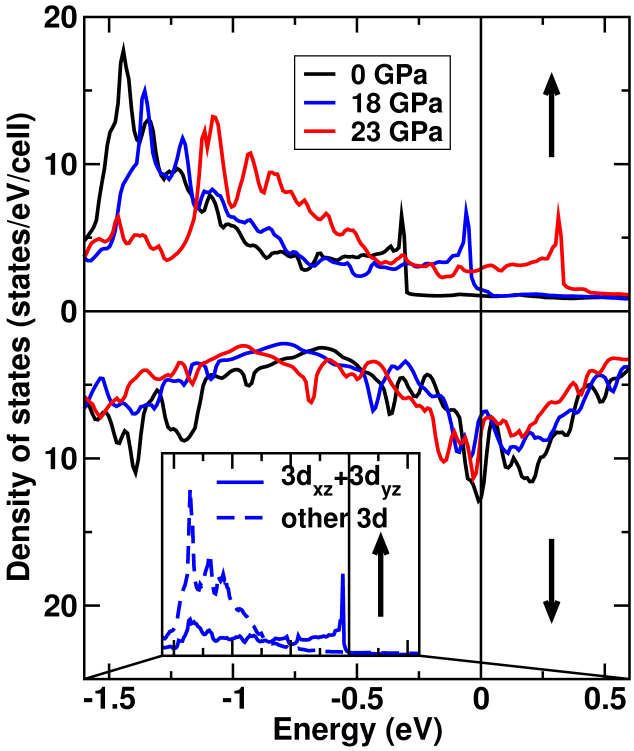


**Fig. 3.** Calculated electronic density of states of $YCo_5$ for different pressures, the different spin directions are marked by arrows. Between 0 GPa (black lines) and 18 GPa (blue lines), only quantitative changes take place related to a slight broadening of the bands due to the decrease of the interatomic distances. If the pressure is raised further, the spin-up states suddenly get partially depopulated (red lines), resulting in the drop of the magnetic moment. The inset shows that the depopulation can be assigned to the Co $3d_{xz}$ and $3d_{yz}$ orbitals, only.

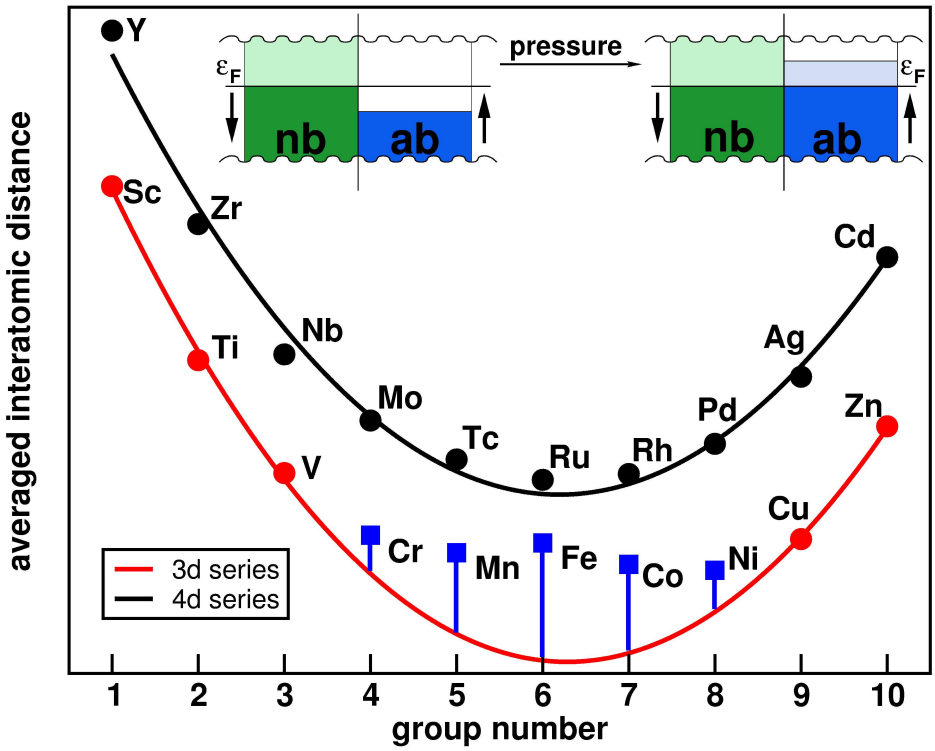


**Fig. 4.** Averaged atomic distance versus group number in the Periodic Table for the $3d$ and $4d$ transition metal series. According to the Friedel model the binding energy, and therefore, the interatomic distances should follow a parabola within each transition metal series. The $4d$ series fulfills this to a good approximation (black curve), whereas in the $3d$ series (red curve) strong deviations occur for all magnetic metals (in blue). This deviation is explained in the left panel of the inset: magnetic order increases the population of the antibonding (ab) majority spins states ($\uparrow$) resulting in a loss of bonding strength. The minority spins ($\downarrow$) states are accordingly depopulated with little influence due to their nonbonding (nb) character. High pressure reverses this effect (right panel) by a depopulation of the (ab) majority spin states resulting in a gain of bonding energy and a loss of magnetic energy and moment.