Magneto-elastic lattice collapse in YCo_5

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The isomorphous collapse of crystalline lattices under pressure is a rare and intriguing phenomenon—the most famous examples being samarium sulphide and cerium metal. Both lattices are cubic under ambient conditions and collapse isomorphically under pressure, remaining cubic with ~15% volume reduction^{1–3}. In SmS the transition results from a change of the 4*f* chemical valence. The collapse in Ce is connected with the altering contributions of the 4*f* electrons to the chemical bonding, the details of which are currently much debated^{4,5}. In contrast, YCo_5 is a hexagonal metallic compound with a stable valence and no 4*f* electrons. Here, we present a combination of high-pressure X-ray diffraction measurements and density functional electronic-structure calculations to demonstrate an entirely different type of isomorphous transition under hydrostatic pressure of 19 GPa. Our results suggest that the lattice collapse is driven by magnetic interactions and can be characterized as a first-order Lifshitz transition, where the Fermi surface changes topologically. These studies support the existence of a bistable bonding state due to the magneto-elastic interaction.

For centuries, phase transitions in solids have played a key role in tailoring material properties, for example, in steel technology. More recently, scientists have been intrigued by isomorphous phase transitions under pressure, where a dramatic change of the electronic structure triggers a volume collapse, while the atomic arrangement in the structure is preserved. Such transitions provide a unique opportunity to study the fundamentals of chemical bonding. In general, high pressure is the most appropriate tool to study the effect of modified atomic distances on physical and chemical 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, whereas external pressure largely 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

Figure 1 The hexagonal crystal structure of YCo_5 . Yttrium atoms in the centre of the hexagons are represented by gold spheres, the two crystallographically non-equivalent cobalt atoms at the corners and on the prism face centres are represented by dark-blue and light-blue spheres.

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 1,400 K, higher than that of any other element or compound. Even under the extreme pressure of 120 GPa the magnetism in Co is only partially suppressed⁷. If diluted with moderate amounts of non-magnetic

Figure 2 Lattice collapse along the hexagonal c axis in YCo_5 under pressures up to 33 GPa. The blue and the red curves show the measured c/a ratios for two different samples at 100 and 140 K, respectively. 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 shows the predicted volume collapse of 1.3% calculated from the equation of states of the low-pressure 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 (the area between the blue curves with open and filled symbols in the transition region). The experimental error bars are smaller than the symbol size.

metals, Co largely retains its strong magnetic properties. The Co-rich intermetallic compounds Y_2Co_{17} (90% Co, $T_C \approx 1,200$ K) and YCo_5 (83% Co, $T_C \approx 1,000$ K) are strong ferromagnets with completely filled majority-spin states in the Co-3d band. This means that the Co spin moment almost retains its maximum atomic value, which is only slightly reduced by hybridization. Compounds of such compositions (SmCo_5 and $\text{Sm}_2\text{Co}_{17}$) are frequently used in permanent-magnet applications⁸. In contrast, YCo_2 (67% Co) shows no spontaneous magnetic order, but becomes ferromagnetic when a strong magnetic field of 69 T is applied⁹.

These facts make YCo_5 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. Previous theoretical studies¹⁰ 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. On the other hand, the isostructural compound ThCo_5 exhibits a metamagnetic transition^{11,12} similar to that in YCo_2 , indicating that YCo_5 may also 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 (ref. 13 and <http://www.fplo.de>; see the Methods section) 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, that is, it preserves the symmetry of both the lattice and the atomic sites (see Fig. 1), the sudden change of lattice parameters is predicted to be significantly anisotropic. Although the atomic distances in the hexagonal plane are almost unaffected, the interplane spacing shrinks considerably.

High-pressure experiments were carried out (see the Methods section) at the European Synchrotron Radiation Facility, Grenoble, to detect the predicted anomaly. The results (see Fig. 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 Fig. 2, where c/a grows with increasing pressure (decreasing volume), belong to the high-moment and low-moment phases, whereas 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 internal 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 the area between the blue curves in the transition region in Fig. 2).

The calculated volume reduction $\Delta V/V = 1.3\%$ agrees well with the experimental value, $\Delta V/V = 1.6 \pm 0.9\%$, although the observed anomalies are less sharp due to small pressure inhomogeneities.

The measured X-ray diffraction patterns (see Supplementary Information, Fig. S2 and Tables S3–S5) show the predicted anomalies of the lattice parameters but no indication of any other structural or symmetry change. Consequently, the transition

Figure 3 Calculated electronic DOS 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.

that YCo_5 undergoes at 19 GPa is an isomorphic first-order phase transition. This is the first observation of a pressure-induced isomorphic volume collapse of an itinerant magnet. A few other systems also exhibit isomorphic transitions under pressure, for example, cerium^{1,2}, samarium sulphide³, barium silicide $\text{Ba}_8\text{Si}_{46}$ (ref. 14), osmium¹⁵ and RFeO_3 perovskites¹⁶. The physical mechanism of the transition in $\text{Ba}_8\text{Si}_{46}$ is unknown, and the transition in Os is not of first order. The mentioned perovskites are antiferromagnetic Mott insulators to be distinguished from the other metallic systems. 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 magneto-elastic interaction, causes the collapse. The related volume change of about 1.6% is smaller than that in Ce or SmS. This is to be expected because magnetic interactions are weak ($T_C \approx 1,000 \text{ K} \approx 0.1 \text{ eV}/k_B$) in relation to the energy 1 eV characteristic of the chemical bond.

At ambient conditions, YCo_5 is a strong ferromagnet like pure cobalt metal, that is, its magnetism is only slightly susceptible to moderate changes of thermodynamic variables. In particular, the magnetic moment is rather stable because 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 ε_F (Fig. 3, upper panel, blue line). As soon as the sharp peak crosses the Fermi level, the majority

Figure 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 fulfils 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-spin states ($\uparrow$) resulting in a loss of bonding strength. The minority-spin ($\downarrow$) states are accordingly depopulated with little influence due to their non-bonding (nb) character. High pressure reverses this effect (right panel) by a depopulation of the antibonding majority-spin states resulting in a gain of bonding energy and a loss of magnetic energy and moment.

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 criterion¹⁷. 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 magneto-elastic coupling, responsible for the transition, can be understood in the framework of the Friedel model^{18,19}. For the non-magnetic $4d$ transition-metal series (Fig. 4, black curve) the successive filling of the bonding, non-bonding and antibonding 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 because it moves the non-bonding states to the Fermi level (Fig. 4, left inset). In contrast, the application of high pressure to YCo_5 favours the elastic part of the energy balance and reduces the magnetic moment. Accordingly the antibonding states are depopulated (Fig. 4, right inset), the system gains additional

bonding energy and the volume shrinks suddenly. Although the balance between magnetic and elastic energy is a general feature, a measurable 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 $\text{Co-}3d_{xz}$ 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.

In 1960, Lifshitz had already predicted that elastic anomalies can occur if the topology of the Fermi surface changes under pressure while preserving the number of valence electrons²⁰. 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 transition²⁰. In the case of YCo_5 , the topology of the Fermi surface changes (see Supplementary Information, Fig. S1) 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 magneto-elastic interaction.

Beyond its fundamental interest²¹, studies of magneto-elastic properties are of major importance for the development of high-tech materials. Magnetic shape-memory alloys^{22,23} exhibit extraordinary magneto-elastic strains and are candidates for actuator or strain-sensor applications. On the other hand, magnetostriction is undesirable in magnetic refrigerants²⁴ where the aim is to minimize hysteretic losses²⁵.

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 1,100 °C for 7 days, followed by crushing and milling to a grain size smaller than 20 μm . 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 wavelength-dispersive electron microprobe.

High pressures were generated using a diamond anvil cell equipped with a samarium-doped strontium borate crystal as a pressure sensor^{26,27} and helium as a pressure-transmitting medium. Diffraction experiments using synchrotron radiation at ID09 (wavelength 41.753 pm) of the European Synchrotron Radiation Facility were carried out 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 the Supplementary Information)²⁸. For the determination of peak positions, indexing of diagrams, and lattice-parameter refinements, the program package WinCSD²⁹ was used.

THEORY

A full-potential non-orthogonal local-orbital (FPLO, release 3.00-5) scheme¹³ was used to obtain highly accurate total energies. In the scalar-relativistic calculations within the local spin-density approximation we used the exchange and correlation potential of Perdew and Wang³⁰. As the basis set, $\text{Co}(3s, 3p, 4s, 4p, 3d, 4d)$ and $\text{Y}(4s, 4p, 4d, 5s, 5p, 5d)$ states were chosen. The lower-lying states were considered as core states that are treated fully relativistically. A k -mesh of 46,656 ($36 \times 36 \times 36$) points in the Brillouin zone was used. Convergence 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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References

1. Bridgman, P. W. The compressibility and pressure coefficient of resistance of ten elements. *Proc. Am. Acad. Arts Sci.* **62**, 207–226 (1927).
2. Bridgman, P. W. The compression of 39 substances to 100,000 kg/cm². *Proc. Am. Acad. Arts Sci.* **76**, 55–70 (1948).
3. Chatterjee, A., Singh, A. K. & Jayaraman, A. Pressure-induced electronic collapse and structural changes in rare-earth monochalcogenides. *Phys. Rev. B* **6**, 2285–2291 (1972).
4. Haule, K., Oudovenko, V., Savrasov, S. Y. & Kotliar, G. The α - γ transition in Ce: A theoretical view from optical spectroscopy. *Phys. Rev. Lett.* **94**, 036401 (2005).
5. McMahan, A. K., Held, K. & Scalettar, R. T. Thermodynamic and spectral properties of compressed Ce calculated using a combined local-density approximation and dynamical mean-field theory. *Phys. Rev. B* **67**, 075108 (2003).
6. Steinle-Neumann, G., Stixrude, L. & Cohen, R. E. Magnetism in dense hexagonal iron. *Proc. Natl Acad. Sci. USA* **101**, 33–36 (2004).
7. Goncharov, A. F., Crowhurst, J. & Zaug, J. M. Elastic and vibrational properties of cobalt to 120 GPa. *Phys. Rev. Lett.* **92**, 115502 (2004).
8. Li, H.-S. & Coey, J. M. D. in *Handbook of Magnetic Materials* Vol. 6 (ed. Buschow, K. H. J.) Ch. 1, 1–83 (North Holland, Amsterdam, 1991).
9. Goto, T., Fukamichi, K., Sakakibara, T. & Komatsu, H. Itinerant electron metamagnetism in YCo_2 . *Solid State Commun.* **72**, 945–947 (1989).
10. Yamada, H. et al. Itinerant-electron metamagnetism of $\text{Y}(\text{Co}, \text{Ni})_5$. *J. Phys. Condens. Matter* **11**, 483–492 (1999).
11. Givord, D., Laforest, J., Lemaire, R. & Lu, Q. Cobalt magnetism in RCO_5 -Intermetallics: onset of 3d magnetism and magnetocrystalline anisotropy ($R = \text{Rare earth or Th}$). *J. Magn. Magn. Mater.* **31–34**, 191–196 (1983).
12. Ballou, R., Shimizu, M. & Voiron, J. Pressure effects on the metamagnetic transition of ThCo_5 . *J. Magn. Magn. Mater.* **84**, 23–28 (1990).
13. Koepnick, K. & Eschrig, H. Full-potential nonorthogonal local-orbital minimum-basis band-structure scheme. *Phys. Rev. B* **59**, 1743–1757 (1999).
14. San Miguel, A. et al. Pressure-induced homothetic volume collapse in silicon clathrates. *Europhys. Lett.* **69**, 556–562 (2005).
15. Ocellil, F. et al. Experimental evidence for a high-pressure isostructural phase transition in osmium. *Phys. Rev. Lett.* **93**, 095502 (2004).
16. Rozenberg, G. Kh. et al. Consequences of pressure-instigated spin crossover in RFeO_3 perovskites: a volume collapse with no symmetry modification. *Europhys. Lett.* **71**, 228–234 (2005).
17. Kübler, J. *Theory of Itinerant Electron Magnetism* Ch. 4.1.1, 158–162 (Clarendon, Oxford, 2000).
18. Söderlind, P., Ahuja, R., Eriksson, O., Wills, J. M. & Johansson, B. Crystal structure and elastic-constant anomalies in the magnetic 3d transition metals. *Phys. Rev. B* **50**, 5918–5927 (1994).
19. Friedel, J. in *The Physics of Metals* (ed. Ziman, J. M.) Ch. 8, 340–409 (Cambridge Univ. Press, New York, 1969).
20. Lifshitz, I. M. Anomalies of electron characteristics of a metal in the high pressure region. *Sov. Phys. JETP* **11**, 1130–1135 (1960).
21. Heathman, S. et al. A high-pressure structure in curium linked to magnetism. *Science* **309**, 110–113 (2005).
22. Murray, S. J., Marioni, M., Allen, S. M., O’Handley, R. C. & Lograsso, T. A. 6% magnetic-field-induced strain by twin-boundary motion in ferromagnetic Ni-Mn-Ga. *Appl. Phys. Lett.* **77**, 886–888 (2000).
23. Sozinov, A., Likhachev, A. A., Lanska, N. & Ullakko, K. Giant magnetic-field-induced strain in NiMnGa seven-layered martensitic phase. *Appl. Phys. Lett.* **80**, 1746–1748 (2002).
24. Pecharsky, V. K. & Gschneidner, K. A. Jr. Giant magnetocaloric effect in $\text{Gd}_5(\text{Si}_2\text{Ge}_2)$. *Phys. Rev. Lett.* **78**, 4494–4497 (1997).
25. Provenzano, V., Shapiro, A. J. & Shull, R. D. Reduction of hysteresis losses in the magnetic refrigerant $\text{Gd}_5\text{Ge}_2\text{Si}_2$ by the addition of iron. *Nature* **429**, 853–857 (2004).
26. Datchi, F., LeToullec, R. & Loubeyre, P. Improved calibration of the $\text{SrB}_3\text{O}_7:\text{Sm}^{2+}$ optical pressure gauge: Advantages at very high pressures and high temperatures. *J. Appl. Phys.* **81**, 3333–3339 (1997).
27. Lacam, A. & Chateau, C. High-pressure measurements at moderate temperatures in a diamond anvil cell with a new optical sensor: $\text{SrB}_3\text{O}_7:\text{Sm}^{2+}$. *J. Appl. Phys.* **66**, 366–372 (1989).
28. Hammersley, A. P., Svensson, S. O., Hanfland, M., Fitch, A. N. & Hausermann, D. Two-dimensional detector software: From real detector to idealised image or two-theta scan. *High Press. Res.* **14**, 235–248 (1996).
29. Akselrud, L. G. et al. Use of the CSD program package for structure determination from powder data. *Mater. Sci. Forum* **133–136**, 335–340 (1993).
30. Perdew, J. P. & Wang, Y. Accurate and simple analytic representation of the electron-gas correlation energy. *Phys. Rev. B* **45**, 13244–13249 (1992).

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Competing financial interests

The authors declare that they have no competing financial interests.

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