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Pressure tuning of charge ordering in iron oxide

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A Verwey-type charge-ordering transition in magnetite at 120 K leads to the formation of linear units of three iron ions with one shared electron, called trimeron. The recently-discovered iron pentoxide (Fe4O5) comprising mixed-valent iron cations at octahedral chains, demonstrates another unusual charge-ordering transition at 150 K involving competing formation of iron trimeron and dimeron. Here, we experimentally show that applied pressure can tune the charge-ordering pattern in Fe4O5 and strongly affect the ordering temperature. We report two charge-ordered phases, the first of which may comprise both dimeron and trimeron units, whereas, the second exhibits an overall dimerization involving both the octahedral and trigonal-prismatic chains of iron in the crystal structure. We link the dramatic change in the charge-ordering pattern in the second phase to redistribution of electrons between the octahedral and prismatic iron chains, and propose that the average oxidation state of the iron cations can pre-determine a charge-ordering pattern.
Iron oxides, composed of two of the most abundant elements in the Earth’s interior, are fundamentally important materials both for basic science and applied technologies\(^1\). The first-known magnetic mineral, magnetite ($\text{Fe}_3\text{O}_4$), was the only simple mixed-valent iron oxide known until recently, and for this reason it is a key model system for investigation of $\text{Fe}^{2+}/\text{Fe}^{3+}$ interplay and related physical phenomena. It was discovered that at 120 K magnetite exhibits an abrupt transition of a metal-insulator-type (the so-called Verwey transition), which is supposed to result from enigmatic charge ordering at the octahedral sites of its cubic spinel structure\(^2\). Numerous studies were aimed to comprehend the nature and mechanisms of this transition\(^3\). Only recently, the elusive charge-ordering pattern in the Verwey phase of magnetite below 120 K was finally solved by means of single crystal X-ray diffraction, and a novel type of quasi-particle consisting of linear units of three iron ions with one shared electron, termed a trimer, was proposed\(^4\). This charge ordering is highly unusual and implies a more intricate underlying phenomenon\(^5\) than ordering of separate $\text{Fe}^{2+}$ and $\text{Fe}^{3+}$ ions that takes place, for example, in $\text{TbBaFe}_2\text{O}_5$\(^6,7\) or charge ordering during the course of charge disproportionation\(^8\).

It was commonly thought that all of the simplest iron oxides fall within three basic stoichiometries, such as $\text{Fe}_2\text{O}_3$, $\text{Fe}_3\text{O}_4$, and $\text{Fe}_5\text{O}_6$. A recent series of high-pressure high-temperature (HP-HT) studies using single crystal X-ray diffraction methods discovered a number of novel iron oxides, e.g., $\text{Fe}_2\text{O}_3$\(^1\), $\text{Fe}_3\text{O}_4$\(^1\), $\text{Fe}_5\text{O}_6$\(^1\), $\text{Fe}_3\text{O}_4$\(^1\), $\text{Fe}_5\text{O}_6$\(^1\), $\text{Fe}_7\text{O}_9$\(^2\), and a new monoclinic polymorph of $\text{Fe}_2\text{O}_3$ which can be stable at ambient conditions\(^3\). Some of the novel oxides, like $\text{Fe}_5\text{O}_6$, $\text{Fe}_7\text{O}_9$, and $\text{Fe}_2\text{O}_3$, were also found to be readily recoverable at ambient conditions. These discoveries open a portal to mixed-valent iron oxides and motivate investigation of their physical properties and potential for emergent innovative applications. $\text{Fe}_3\text{O}_4$ can be synthesized at moderate HP-HT conditions of about 10 GPa and 1000 °C and has appeared to be the most common of the above high-pressure iron oxides. It crystallizes in an orthorhombic $\text{CaFe}_{2}\text{O}_4$-type structure, one of the known ferrite ($\text{CaFe}_{2}\text{O}_4$, $n = 1, 2, 3, \ldots$) phases\(^24,25\), and this fact could explain the phase and chemical stability of $\text{Fe}_3\text{O}_4$ and its derivatives, (M,$\text{Fe})_2\text{Fe}_2\text{O}_5$ ($\text{M} = \text{Mg, Cr, Mn}$)\(^26-31\) at ambient conditions. The crystal structure of $\text{Fe}_3\text{O}_4$ comprises chains of both trigonal prisms Fe1 (this crystallographic position is denoted here as Fe1) with shared triangular faces, occupied by $\text{Fe}^{2+}$ cations, and an octahedral network occupied by mixed $\text{Fe}^{2+}/\text{Fe}^{3+}$ cations and consisting of (i) single chains of octahedra sharing opposite edges (this crystallographic position is denoted here as Fe2), and (ii) double chains of octahedra composed of two chains similar to the above Fe2 ones, but attached together side-by-side via two other octahedron edges (this crystallographic position is denoted here as Fe3)\(^12\). Like magnetite, $\text{Fe}_3\text{O}_4$ shows a charge-ordering transition below 150 K involving the competing formation of iron trimers and dimers (two Fe ions with one shared electron) at the octahedral network\(^32\). It is interesting to note that a recent study identified coexisting trigonal and dimer-like charge ordering patterns in layered $\alpha$-$\text{RuCl}_3$\(^33\).

In this work, we synthesize high-quality single crystals of $\text{Fe}_7\text{O}_9$ and investigate the effect of high pressure on charge ordering in $\text{Fe}_7\text{O}_9$ at low temperature using single crystal X-ray diffraction, Mössbauer spectroscopy, and magnetization measurements. We find that cold compression of $\text{Fe}_7\text{O}_9$ stimulates electron transfer between iron cations of different coordination and leads to the formation of novel charge-ordered phases.

Results

Phase III and two options for its crystal structure. In all experiments, we start from normal conditions ($\text{Fe}_7\text{O}_9$-I phase) (Figs. 1a and 2) and gradually decrease the temperature in the cryostat. At about 200 K and 2 GPa, we observe the appearance of weak and blurred superlattice reflections, indicating the emergence of scattered fragments of a charge-ordering pattern (Fig. 3b). With further temperature decrease and pressure increase, these reflections become progressively stronger and clearer (Fig. 3c). We verify that these reflections do not belong to the earlier-reported charge-ordered $\text{Fe}_7\text{O}_9$-II phase\(^32\), and label this phase as $\text{Fe}_7\text{O}_9$-III. Meanwhile, the presence of $\text{Fe}_7\text{O}_9$-II is noticeable at 5–7 GPa at the lowest temperature point of 30 K (Fig. 2). Upon heating at about 18 GPa, we can follow the superlattice reflections of $\text{Fe}_7\text{O}_9$-III up to at least 270 K (Fig. 2). Thus, pressure strongly enhances the temperature of the charge-ordering transition, compared to 150 K at ambient pressure\(^32\).

We can index the single-crystal diffraction patterns of $\text{Fe}_7\text{O}_9$-III in either orthorhombic or monoclinic unit cells (Fig. 3d). Eventually, we determine two candidate crystal structures, namely, $\text{Fe}_7\text{O}_9$-III-a with a monoclinic $C2/m$ lattice (Fig. 4) and $\text{Fe}_7\text{O}_9$-III-b with an orthorhombic $C22\text{I}$ unit cell (Fig. 5), which can equally well fit the experimental X-ray diffraction patterns (Table 1 and Supplementary Table 1). Compared to the original structure ($\text{Fe}_7\text{O}_9$-I), the crystallographic sites of the iron cations occupying the trigonal prisms in the crystal structures of both $\text{Fe}_7\text{O}_9$-III-a and $\text{Fe}_7\text{O}_9$-III-b are split into two slightly non-equivalent Fe1_1 and Fe1_2 positions; likewise the octahedral sites Fe2 and Fe3 are split into multiple non-equivalent sites, highlighted in different colors in Figs. 4 and 5. Note here that the unusual incommensurately-modulated character of the crystal structure of $\text{Fe}_7\text{O}_9$-II, reported in previous works\(^32\), could result from a lattice instability related to competition between the $\text{Fe}_7\text{O}_9$-III-a and $\text{Fe}_7\text{O}_9$-III-b phases. A similar type of incommensurability was observed, for example, in the spin-Peierls compound, Ti$\text{PO}_4$\(^34,35\).

In magnetite, the formation of iron trimers in its charge-ordered phase is perfectly traced by anomalous shortening of some Fe–Fe distances as found by single crystal X-ray diffraction method\(^4\); hence we also apply this approach to $\text{Fe}_7\text{O}_9$. The octahedral chains occupied by mixed-valent iron cations show pronounced shortening of distances between some neighboring Fe atoms; whereas the prismatic chains of iron in both $\text{Fe}_7\text{O}_9$-III-a and $\text{Fe}_7\text{O}_9$-III-b structures are characterized by nearly equal...
Fe–Fe distances. For example, at 11.7 GPa and 180 K, the Fe–Fe distances in the prismatic chains of the Fe₄O₅-III-a structure show a periodicity consisting of one 2.8143 Å and two 2.8176 Å distances; since these two values are very similar, we cannot draw any conclusions about the formation of coupled units in these chains. Compared to the average Fe–Fe distance of ~2.8165 Å along the same crystallographic direction (b-axis), the distances between two neighboring octahedrally-coordinated Fe₂⁻⁻ atoms in the single chains of Fe₂ octahedra are reduced, to 2.6597 Å, and likewise those between Fe₃⁻⁻ atoms in the double chains of Fe₃ octahedra are reduced to 2.7279 Å (Supplementary Table 2). These dramatic shortenings in the distances suggest the formation of dimers (Fig. 4a, c). In the other octahedral chains of this Fe₄O₅-III-a phase, equal contractions in two neighboring Fe–Fe distances indicate the formation of trimers.

The Fe₄O₅-III-b structure exhibits similar features. Its prismatic iron chains show a periodicity in the Fe–Fe bond lengths consisting of one 2.8118 Å and two 2.8189 Å distances, where the difference between the two is too small to allow any conclusions about the formation of any bonded units (Fig. 5). In contrast to Fe₄O₅-III-a, the Fe₄O₅-III-b structure does not contain any trimers (Fig. 5). Both octahedral chains of the Fe₄O₅-III-b structure exhibit only dimers with a Fe–Fe bond length of 2.6777 Å in the single chains of Fe₂ octahedra, and 2.7387 Å in the double-chains of Fe₃ octahedra (Supplementary Table 2). Both Fe₄O₅-III-a and Fe₄O₅-III-b crystal structures show a strong rapprochement between free Fe₃ atoms (Fe₃⁻⁻ in phase III-a and Fe₃⁻⁻ in phase III-b, which are unincorporated into the dimer and trimer units) and the neighboring Fe₁ atoms in the prisms, which are connected to these Fe₃ octahedra via one shared edge (these Fe₃⁻⁻–Fe₁ pairs are highlighted as white dashed ellipsoids in Figs. 4da and 5d).

Fig. 2 High-pressure low-temperature phase diagram of Fe₄O₅. The diagram is based on the single crystal X-ray diffraction experiments. Experimental points on the diagram corresponding to different phases are shown in different symbols. The shaded areas show the proposed stability regions of the phases. The lines and arrows show the directions of the pressure and temperature variation during the experiments. Since the basic structural reflections of Fe₄O₅-I and Fe₄O₅-III structures are identical (Fig. 3), the region of their co-existence could not be properly delineated. One cannot rule out that the region of Fe₄O₅-III in the phase diagram might be a superposition of stability ranges of Fe₄O₅-III-a and Fe₄O₅-III-b phases.

Fig. 3 Examples of reciprocal lattice planes (hkl) of Fe₄O₅. These plots correspond to different pressure and temperature conditions (indicated for each plot). a Basic reflections corresponding to the original Fe₄O₅-I structure, highlighted by red circles. b, c Emergence of superlattice reflections, highlighted by blue circles (in b these reflections are rather weak and blurred, but in c they are strong and clear). d Reconstruction of (hkl) reciprocal lattice planes, which reveals two possible unit cells of Fe₄O₅-III. The first option is an orthorhombic C-centered “average” cell, shown in the upper left corner together with its modulation wave vector q (Fe₄O₅-III-b). The second option is a C-centered unit cell with a tripped lattice parameter a, compared to the average cell (Fe₄O₅-III-a), highlighted at the bottom of the plot.
Phase IV and charge ordering in chains of trigonal prisms. In all three experimental runs at pressures above 12 GPa and temperatures below 150 K, we observe the appearance of additional structural reflections (Supplementary Fig. 1), suggesting the beginning of another transition to a further phase, labeled as Fe₄O₅-IV (Fig. 2). Below 150 K this transition is nearly complete at 25 GPa, but at slightly higher temperature (200 K), minor traces of Fe₄O₅-III are still observable even at 36 GPa (Fig. 2). Upon heating to room temperature at 36 GPa, Fe₄O₅-IV gradually transforms to the original Fe₄O₅-I phase; meanwhile, a noticeable fraction of Fe₄O₅-IV persists even at 293 K (Fig. 2).

The single crystal X-ray diffraction images of Fe₄O₅ collected at 25.2 GPa and 120 K correspond to almost pure Fe₄O₅-IV (Supplementary Fig. 1), and we determine its monoclinic P₂₁/m symmetry and atomic positions. The structure shows an overall dimerization along the c-axis involving both octahedral and prismatic chains (Fig. 6). We calculate BVS values of the iron ions in this structure using the above method, and find an average value for the prismatic Fe1 atoms of +2.26. This value deviates from +2 established for these prismatic sites in the original Fe₄O₅-I phase, and taking into account the emergence of dimeric ordering in these chains, we conclude that the prismatic sites in Fe₄O₅-IV are filled with mixed-valent iron cations. In the same way, the average BVS values of the iron in the single chains of Fe2 and double chains of Fe3 octahedra in Fe₄O₅-IV are found as +2.63 and +2.554, respectively (Fig. 6). These values are also consistent with the dimeric ordering in the chains. These BVS results indicate that Fe₄O₅ with a nominal average oxidation state of iron as Fe².⁵⁺ tends to reach a state under pressure with more uniform charge distribution, implying an average oxidation state of Fe².⁵⁺ in all iron chains.

During the Fe₄O₅-III → Fe₄O₅-IV phase transition under increasing pressure, the crystal lattice shrinks noticeably along
the dimerization direction. This leads to a lattice volume collapse by about 0.5% at 120 K (Fig. 7a). This volume collapse may be attributed to a more homogeneous charge distribution in the Fe4O5-IV phase, which should lead to a volume contraction. By fitting the third-order Birch–Murnaghan equation of state37,38 to the compression data of the Fe4O5-III phase at 120 K (Fig. 7a), we determine the unit cell volume as $V_0 = 1063.87 \, \text{Å}^3$ and the bulk modulus as $B_0 = 195.3 \, \text{GPa}$ for fixed $B'_0 = 4$. We analyze the ratios of Fe–Fe bond lengths in the dimer units compared to those in the gaps between them ($\frac{\Delta \text{Fe–Fe}_{\text{units}}}{\Delta \text{Fe–Fe}_{\text{dop}}}$) for Fe1, Fe2, and Fe3 chains, and values to be 0.93, 0.90, and 0.88, respectively (Supplementary Table 4). This difference in the ratios may be referred to the above average BVS values of Fe1, Fe2, and Fe3 atoms, which should approximately correspond to their oxidation states. In fact, the shortest iron dimers are formed in the double chains of Fe3 octahedra with an average BVS value

![Fig. 5 Orthorhombic crystal structure of Fe₄O₅-III-b.](image)

**Table 1 Unit cell parameters of different phases of Fe₄O₅**

| Details of crystal structures | Phases                         | Fe₄O₅-I          | Fe₄O₅-III-a       | Fe₄O₅-III-b       | Fe₄O₅-IV (LT)       | Fe₄O₅-IV (HT)       |
|-------------------------------|-------------------------------|------------------|-------------------|-------------------|-------------------|-------------------|
| Pressure (GPa)                | Ambient                       | 11.7             | 11.7              | 25.2              | 48                |
| Temperature (K)               | 293                           | 180              | 180               | 120               | 296               |
| Crystal system                | Orthorhombic                  | Monoclinic       | Orthorhombic      | Monoclinic        | Monoclinic        |
| Space group (No.)             | Cmcm (No. 63)                 | C2/m (No. 12)    | C222 (No. 20)     | P21/m (No. 11)    | P21/m (No. 11)    |
| Lattice parameter, $a$ (Å)    | 2.89200(5)                    | 9.675(4)         | 8.4492(3)         | 12.1155(18)       | 11.7880(18)       |
| Lattice parameter, $b$ (Å)    | 9.7979(2)                     | 8.4493(3)        | 9.6750(4)         | 12.1155(18)       | 11.7880(18)       |
| Lattice parameter, $c$ (Å)    | 12.583(2)                     | 12.328(7)        | 12.328(7)         | 5.4282(4)         | 5.3287(4)         |
| $\beta$ (°)                  | 90.0(1)                       | 90.0(1)          | 90.0(1)           | 90.0(1)           | 90.0(1)           |
| Unit cell volume, $V$ (Å³)    | 356.54 (7)                    | 1007.8 (6)       | 1007.7 (6)        | 317.66 (8)        | 299.33 (8)        |
| $Z$                           | 4                             | 12               | 12                | 4                 | 4                 |
| Calculated density (g/cm³)    | 5.65138                       | 5.99868          | 5.99875           | 6.34361           | 6.73215           |

*This phase appeared after laser heating.
Fig. 6 Monoclinic crystal structure of Fe₄O₅-IV. The structure has P2₁/m symmetry and plots are based on the crystal structure data refined at 25.2 GPa and at 120 K. a Projection of the trigonal prisms Fe₁ and single chains of Fe₂ octahedra. b Two unit cells projected down the c-axis. Thin solid lines indicate the unit cell edges. c Projection of the double chains of Fe₃ octahedra. d Projection down the b-axis of one of the two diagonal ribbons shown in e. e Two characteristic diagonal ribbons consisting of five iron chains each. f Projection down the b-axis of one of the two diagonal ribbons shown in e. Solid ellipsoids are dimers formed in all iron chains. Different crystallographic positions are shown in different colors. g Bond valence sums (BVS) values of all the iron cations in the crystal structure.

Fig. 7 Pressure-driven Fe₄O₅-III → Fe₄O₅-IV transition. a Equation of state of Fe₄O₅ at 120 K showing a volume drop of ~0.5% at the Fe₄O₅-III → Fe₄O₅-IV transition. b Edge-shared diagonal ribbons of prisms and octahedra (seen in Figs. 4–6) provide channels for charge hopping between the prisms and octahedra. c Correlation between ratios of Fe–Fe distances in dimers and trimers to those in gaps between them (d_{Fe–Fe}^{min}/d_{Fe–Fe}^{gap}) and absolute deviations of bond valence sums (BVS) values of iron in these chains from 2.5+. d Model demonstrating the coexistence of several charge-ordered phases in a single crystal of Fe₄O₅. The electron transfer from the prisms to octahedra leads to a short-range reorganization of ordering type.
equal to +2.554, i.e., nearly optimal for the formation of Fe$^{2+}$–Fe$^{3+}$ pairs. In contrast, the longest dimers are formed in Fe1 prismatic chains with an average BVS value of +2.26, which deviates the most from +2.5. Furthermore, we note that the above $\dfrac{d_{\text{Fe}-\text{Fe}}}{\text{Fe}^{2+}/\text{Fe}^{3+}}$ ratios increase linearly with a deviation of their average BVS values from +2.5, tending to 1 for the limiting case of Fe$^{2+}$ or Fe$^{3+}$ (Fig. 7c). This regularity indicates that the resulting length of the dimers is determined by the balance of Fe$^{2+}$ and Fe$^{3+}$ cations in each linear chain. The reduced distances between the free Fe3 atoms in the double-chains of Fe3 octahedra and the neighboring Fe1 atoms in the prisms, observed in both FeO$_5$-III-a and FeO$_5$-III-b structures (highlighted as dashed ellipsoids in Figs. 4d and 5d), appear to be the most suitable channels for hopping of electrons from Fe$^{2+}$ ions occupying Fe1 prisms to the octahedral matrix. Only 1/3 of the Fe1 atoms are involved in these channels, and hence, if the electrons of prismatically-coordinated Fe$^{2+}$ ions are not delocalized within the framework of these trigonal prismatic chains, the Fe1 atoms may be maximally charged up to +2.33 on average. The actual BVS values of the two Fe1 atoms are +2.23 and +2.29 (Fig. 6), which satisfy this constraint well. The coexistence of FeO$_5$-III and FeO$_5$-IV phases over an extended pressure range (Fig. 2) suggests that this phase transition is rather prolonged. Likely, it is caused by the gradual pressure-driven electron transfer from the trigonal prismatic chains to the octahedral ones. The FeO$_5$-III-b structure comprises only dimers; hence having free iron cations in all Fe3 chains provides twice as many channels for the charge hopping compared to the FeO$_5$-III-a structure.

As mentioned above, we observe that a noticeable fraction of the Fe$_2$O$_4$-IV phase persists upon heating to 293 K at 35 GPa (Fig. 2). To examine the possibility of the room-temperature phase transition Fe$_2$O$_4$-I $\rightarrow$ Fe$_2$O$_4$-IV, we compress a single crystal of Fe$_2$O$_4$ in a separate experiment to about 45 GPa, but we see no evidence for a phase transition. Previous works also did not find any structural phase transition in this range.12,39 At the maximum pressure of 45 GPa, we laser-heat the sample up to 2000 °C, and indeed we observe a structural transition to the same dimerized Fe$_2$O$_4$-IV structure (Fig. 2, Table 1). The unusual thermodynamic stability of the FeO$_5$-IV phase might be explained by the fact that both FeO$_5$-III-a and FeO$_5$-III-b low-temperature structures have the above-discussed Fe3–Fe1 channels for charge hopping (Figs. 4d and 5d), which should facilitate the FeO$_5$-III $\rightarrow$ FeO$_5$-IV transition; whereas a direct FeO$_5$-I $\rightarrow$ FeO$_5$-IV transition and its related redistribution of electrons between the prismatic and octahedral chains might be hindered at room temperature, but triggered at high temperatures. We find that average BVS values of the iron ions in the high-temperature FeO$_5$-IV (HT) phase are nearly the same as those in the low-temperature FeO$_5$-IV (LT) phase, namely, +2.24 (+2.32) for prismatic Fe1$_1$ (Fe1$_2$) atoms, and +2.653 and +2.534 for the iron in the single chains of Fe2 and double chains of Fe3 octahedra, respectively. Analysis of $\dfrac{d_{\text{Fe}-\text{Fe}}}{\text{Fe}^{2+}/\text{Fe}^{3+}}$ ratios in the FeO$_5$-IV (HT) structure shows that they do not follow the linear trend established for the FeO$_5$-IV (LT) structure (Fig. 7c), and hence a distribution of Fe$^{2+}$ and Fe$^{3+}$ ions at least at the octahedral sites of FeO$_5$-IV (HT) is more random than ordered. It can be that the transition mechanism at high temperature is different, and the dimerization observed could instead result from a Peierls transition rather than from the formation of electrically-bonded Fe$^{2+}$–Fe$^{3+}$ dimers with a shared electron.

Low-temperature high-pressure phase diagram of Fe$_2$O$_4$. We find the average BVS values of prismatic Fe1 atoms in FeO$_5$-I, FeO$_5$-III-a, FeO$_5$-III-b, and FeO$_5$-IV to be +2.016, +2.11, +2.13, and +2.26, respectively (Figs. 4–6). As discussed above, the average BVS value of +2.26 for Fe1 atoms in FeO$_5$-IV, together with the overall structural dimerization including these Fe1 chains, unambiguously confirm the mixed-valent nature of the iron ions at the prismatic sites in this structure. The minor deviations of the BVS values from +2 for Fe1 atoms in the FeO$_5$-III-a and FeO$_5$-III-b phases do not allow us either to conclude a small shift in the oxidation state of these ions toward +3 or to rule that out. The co-existence of FeO$_5$-III and FeO$_5$-IV phases for an extended pressure range (Fig. 2) hints that this transition may follow the electron transfer between the octahedral and prismatic chains. This leads to a short-order reorganization of the charge-ordering pattern and the formation of inclusions of the novel structural order. Comparing the different charge-ordered patterns in FeO$_5$-III32, FeO$_5$-III-a, FeO$_5$-III-b, and FeO$_5$-IV (Figs. 4–6), we conclude that the average oxidation state of octahedrally-coordinated cations predetermines which ordering type would be optimal. For example, in order to form short trimers, the average oxidation state of iron should be $\sim$+2.7 (Fig. 7c). A moderate decrease in this BVS value leads to the formation of more loosely-bonded long trimers and dimers. For BVS values tending toward +2.5, a closely-packed dimeric order becomes preferable (Fig. 6). Thus, the average oxidation state of the iron ions at the octahedral chains apparently pre-determines an optimal charge-ordering scheme. One can expect, for example, in the newly-discovered Fe$_2$O$_4$ and Fe$_3$O$_4$ crystallizing in similar structures14,22, that the former with a nominal oxidation state of the octahedral ions of +2.8 at ambient pressure is prone to the formation of exclusively trimers; likewise, the latter in which their oxidation state is +2.5 is prone to dimer formation only. A pressure-stimulated electron transfer from the prismatic to octahedral chains can occur inhomogeneously in the bulk of the Fe$_2$O$_4$ crystal and this can result in the formation of an anomalous charge-ordering pattern combining different co-existing ordering schemes (Fig. 7d).

The process of electron transfer in Fe$_2$O$_4$ from the trigonal prismatic to the octahedral iron chains towards charge equalization is perhaps not complete by 40 GPa, and with further pressurization the average BVS values of all iron cations can probably approach +2.5 even more closely. However, this could hardly change the dimeric charge-ordering pattern of FeO$_5$-IV (Fig. 6), unless the material was to become metallic and the charge-ordering state suppressed; although the lattice symmetry may be sensitive to the charge balance. We propose that such electron transfer processes under pressure could also occur in other iron oxides crystallizing in kindred lattices, like the above-mentioned Fe$_2$O$_4$ and Fe$_3$O$_4$, however, for the ambient-pressure cubic spinel phase of magnetite with inverse electronic configuration in which tetrahedral sites are filled by Fe$^{3+}$ ions and hence are already maximally charged, the possibility of an opposite electron transfer under pressure, from tetrahedral sites to the octahedral network has been suggested41. However, this conjecture was not in line with earlier work42, and was not confirmed in subsequent studies43–46. It was established for magnetite that its charge-ordered phase may be suppressed by applied pressure of about 8 GPa47.48. Thus, the behavior of Fe$_2$O$_4$ is remarkably different from that of magnetite and demonstrates new perspectives for charge-ordered states in iron-rich oxides. At the moment, we cannot unambiguously ascertain the driving forces of the phase transitions observed in Fe$_2$O$_4$ both at ambient and high pressures. In previous work investigating the Verwey transition in magnetite, it was determined that the intersite Coulomb interactions between the 3d electrons of the Fe ions alone, as well as phonon-driven lattice instability, could hardly stimulate this transition49,50. A more complex scenario, however, in which the strong electron correlations enhance the electron–phonon interactions and simultaneously reduce the mobility of the minority-spin $t_{2g}$ electrons of Fe$^{2+}$ ions,
increasing their tendency towards localization, could be an indication that electron–phonon interactions may be a driving force of the Verwey transition\textsuperscript{49,50}. The phase transitions in Fe\textsubscript{3}O\textsubscript{4} could have similar or even more complex scenarios involving the charge, lattice, spin, and orbital degrees of freedom.

Mössbauer spectroscopy of Fe\textsubscript{4}O\textsubscript{5} at low temperature under high pressure. At ambient conditions, the Mössbauer spectra of Fe\textsubscript{4}O\textsubscript{5} can be well fitted by the superposition of a magnetic sextet and a paramagnetic doublet with relative areas of 80(2)% and 20(2)%, respectively (Fig. 8c). The presence of the sextet component indicates the existence of magnetic order at room temperature. In the Fe\textsubscript{4}O\textsubscript{5} crystal, 25% of iron cations occupy the trigonal prisms, and 75% have octahedral coordination (Fig. 1a). Hence, we can assign the doublet to prismatic Fe\textsubscript{1} atoms, and likewise the sextet to octahedral Fe\textsubscript{2} and Fe\textsubscript{3} atoms. We determine the hyperfine parameters of these components. For example, for the spectrum collected at 295 K and 2.1 GPa, we determine the center shift of the doublet to be \( \delta_{\text{CS}} = 1.125(12)\) mm/s and the quadrupole splitting to be \( \Delta = 1.93(2)\) mm/s. For the sextet, the center shift is \( \delta_{\text{CS}} = 0.568(15)\) mm/s, the quadrupole shift to be \( \epsilon = 0.21(1)\) mm/s, and the hyperfine magnetic field to be \( H_{\text{hf}} = 24.96(13)\) T. The center shift of the Mössbauer spectral components depends primarily on the oxidation state of iron in a linear-like manner. We compare these center shifts with those reported for other iron oxides, e.g., \( \delta_{\text{CS}} = 0.36\) mm/s for octahedral Fe\textsuperscript{3+} ions in hematite (α-Fe\textsubscript{2}O\textsubscript{3})\textsuperscript{51} and \( \delta_{\text{CS}} = 0.67\) mm/s for octahedral mixed-valent Fe\textsuperscript{2.5+} ions in magnetite\textsuperscript{51}. The linear trend based on these data suggests that octahedrally-coordinated Fe\textsuperscript{2+} ions should exhibit center shifts around \( \delta_{\text{CS}} = 0.98\) mm/s; likewise the above-mentioned center shift of \( \delta_{\text{CS}} = 0.568\) mm/s for the magnetic sextet in Fe\textsubscript{4}O\textsubscript{5} should correspond to an oxidation state of Fe\textsuperscript{2.67+}, in excellent agreement with the BVS results (Fig. 1a). The large value of \( \delta_{\text{CS}} = 1.125(12)\) mm/s for the Fe\textsubscript{1} doublet unambiguously corresponds to Fe\textsuperscript{2+}, in line with both BVS estimations (Fig. 1a) and earlier data for ferrous-iron compounds\textsuperscript{51}.

We note that the line widths of the sextet are roughly twice as large as those of the doublet (1.1 vs 0.5 mm/s) (Fig. 8c). This broadening results from electron exchange between the Fe\textsuperscript{2+} and Fe\textsuperscript{3+} cations occupying the octahedral sites; a similar effect was also observed in magnetite\textsuperscript{52}. Upon cooling, the doublet component loses intensity and completely disappears around 150 K (Fig. 8b). Hence, Fe\textsubscript{1} atoms occupying the oxygen prisms become magnetically ordered, and their contribution to the spectra largely overlaps with the stronger signal of Fe\textsubscript{2} and Fe\textsubscript{3} atoms. The Mössbauer spectra demonstrate a pronounced broadening around 150 K (Fig. 8b), where a charge ordering in Fe\textsubscript{3}O\textsubscript{4} was observed\textsuperscript{32}.

For magnetite, it has been documented that charge ordering below the Verwey transition at 120 K leads to the appearance of many closely-overlapping magnetic sextets which can be resolved only under special conditions, such as single-crystal measurements in magnetic fields\textsuperscript{52,53}. Here, we collect spectra from a polycrystalline Fe\textsubscript{3}O\textsubscript{4} sample and, together with other factors like potential phase co-existence (Fig. 2), this impedes an unambiguous fitting of the Mössbauer spectra at low temperatures. A simple single-sixtet analysis of the spectra shows that the quadrupole shift has a discontinuity in its temperature dependence between 150 and 100 K (Supplementary Figure 2b and Supplementary Table 5). This feature is likely linked to changes in the magnetic properties (kink in inverse magnetic susceptibility in Fig. 7a).

The Mössbauer spectra collected in the charge-ordered states appear to be a superposition of several sextets. For instance, the spectrum acquired at 20 K and 2.6 GPa, i.e., in the stability region of the incommensurately-modulated Fe\textsubscript{4}O\textsubscript{5}-II phase with an infinite number of different environments for iron (Fig. 2), can be reasonably well described by three sextets (Fig. 8c). The center shifts of these sextets are about 0.6–0.85 mm/s, i.e., between \( \delta_{\text{CS}} = 0.36\) mm/s for Fe\textsuperscript{3+} ions in hematite\textsuperscript{51} and 0.98 mm/s estimated above for octahedral Fe\textsuperscript{2+} atoms, but at the same time quite far from both. We therefore conclude that in the charge-ordered phases of Fe\textsubscript{3}O\textsubscript{4}, the oxidation states of the octahedrally-coordinated iron did not split into Fe\textsuperscript{2+} and Fe\textsuperscript{3+} components, and hence, these ions are characterized by stable non-integer oxidation states. This finding is in line with the earlier conjecture\textsuperscript{43,44} that the minority-spin \( \text{Fe}_2^+ \) electron of Fe\textsuperscript{2+} is shared between all ions involved in the formation of either trimers or dimers.

We do not observe any noticeable changes in the spectra with pressure up to 8 GPa at low temperatures. This fact indicates that Fe\textsubscript{3}O\textsubscript{4}-II and Fe\textsubscript{3}O\textsubscript{4}-III charge-ordered phases are not readily distinguishable by Mössbauer spectroscopy (Figs. 2 and 8c). With further compression to 16.3 GPa across the beginning of the Fe\textsubscript{3}O\textsubscript{4}-III → Fe\textsubscript{3}O\textsubscript{4}-IV transition (Fig. 2), the hyperfine field distribution changes to an apparent bimodal form (Supplementary Figure 2c). We fit these spectra by a superposition of two sextets (Fig. 8c), and for example, at 11.3 GPa and 20 K in Fe\textsubscript{3}O\textsubscript{4}-III phase, their center shifts are \( \delta_{\text{CS}} = 0.66(3) \) and 0.82 (3) mm/s. Taking into account the second-order Doppler shift (we use the value of 0.11 mm/s for hematite)\textsuperscript{54} and disregarding a possible pressure correction for the \( \delta_{\text{CS}} \) values, we estimate the average oxidation states of iron linked to the green and purple sextets to be +2.7 and +2.45, respectively (Fig. 8c). Therefore, this case also unambiguously demonstrates that the oxidation states of the octahedrally-coordinated iron in Fe\textsubscript{3}O\textsubscript{4} do not split into integer Fe\textsuperscript{2+} and Fe\textsuperscript{3+} components, even at 20 K. These +2.7 and +2.45 values correspond well to the average BVS values for the iron cations occupying the single chains of Fe\textsubscript{2} and double chains of Fe\textsubscript{3} octahedra, respectively (Figs. 4 and 5).

Magnetic properties of Fe\textsubscript{4}O\textsubscript{5}. The magnetization data for Fe\textsubscript{4}O\textsubscript{5} collected at ambient pressure (Fig. 8a) are similar to those reported earlier\textsuperscript{32}, but show slightly smaller absolute values of susceptibility. In this work, we carry out measurements on several single crystals of Fe\textsubscript{4}O\textsubscript{5}, and likely, this discrepancy may be related to a minor ferromagnetic impurity which can potentially be present in the large polycrystalline sample examined earlier\textsuperscript{32}. There are two main features of the magnetization data: (i) the transformation between canted and collinear magnetic ordering (around 90 K at ambient pressure), and (ii) charge ordering that manifests itself by a kink in the 1/\( \chi \) curve (around 150 K at ambient pressure) (Fig. 8a). Both features are observed up to 1.83 GPa, the maximum pressure of our measurement, and shift toward higher temperature upon compression. The size of the canted moment increases abruptly, with a large change between 0.66 and 0.90 GPa and weak changes below or above this range. Given the observation of the Fe\textsubscript{4}O\textsubscript{5}-III phase at 200 K and 2 GPa (Fig. 2), we conclude that our magnetization data extend well into its stability range, and hence, this abrupt change in the moment likely results from the phase transformation. Moreover, the kink in the 1/\( \chi \) curves shifts to higher temperatures (Fig. 8a), in agreement with the positive slope of the Fe\textsubscript{4}O\textsubscript{5}-II → Fe\textsubscript{4}O\textsubscript{5}-III phase boundary. Above 0.90 GPa, the kink is strongly smeared out, probably because of more sluggish charge-ordering processes at the Fe\textsubscript{4}O\textsubscript{5}-I → Fe\textsubscript{4}O\textsubscript{5}-III phase transition, compared to Fe\textsubscript{4}O\textsubscript{5}- II → Fe\textsubscript{4}O\textsubscript{5}-III\textsuperscript{32}.

The magnetization data reveal close similarities between Fe\textsubscript{3}O\textsubscript{4}-II and Fe\textsubscript{3}O\textsubscript{4}-III. Both support the formation of a canted state at low temperatures. Moreover, both charge-ordered phases emerge from the same collinear magnetic order that sets in around 320 K at ambient pressure\textsuperscript{32}. As seen from the Mössbauer
spectra (Fig. 8b), the initial magnetic ordering remains above room temperature at these pressures. As established earlier32, a ferromagnetic spin alignment along the a-direction (in the coordinate framework of Fe₄O₅-I) is essential for the formation of dimers and trimers in the charge-ordered state32, and hence magnetic ordering is a key prerequisite of the charge ordering. The same type of magnetic order would even support dimer formation in Fe₄O₅-IV. This demonstrates that this magnetic ordering can produce different charge-ordered states in a single structural framework.

Conclusions. We determined the low-temperature high-pressure phase diagram of Fe₄O₅ using single crystal X-ray diffraction and Mössbauer spectroscopy and by measurement of magnetic properties. We found two novel crystal structures of Fe₄O₅ and observed the extended regions of their co-existence in the phase diagram. A dramatic change in the charge-ordering pattern in the second high-pressure phase was attributed to electron hopping from the octahedral to the prismatic iron chains. We propose that the average oxidation state of the iron cations in oxides of this family can pre-determine a charge-ordering pattern. Thus, Fe₄O₅ demonstrates that the charge-ordering pattern can be changed by applied pressure or stress, and two or more charge-ordered phases can co-exist with each other inside one single crystal. Our work highlights the complexity of charge-ordering processes in iron-based and other transition metal oxides, but simultaneously it suggests a clue to these phenomena.

Methods
Sample preparation and characterization. The samples of Fe₄O₅ were synthesized in a 120-tonne Multi-Anvil Press at BGI55 at HP-HT conditions from stoichiometric mixtures of fine powders of Fe₂O₃ (Aldrich, 99.99% purity) and Fe (Aldrich, 99.999% purity). The syntheses were performed at pressures of 14 GPa over several hours.
Polycrystalline samples were fabricated at synthesis temperatures of about 1100–1200 °C, while higher temperatures (1350–1450 °C) enabled the growth of high-quality single crystals with linear sizes of 20–200 µm. We employed a standard assembly including a Re cylindrical sample capsule, a La2O3 heater, a W3Re/W25Re thermocouple, and other components packed inside an octahedron made of 5% Cr2O3-doped MgO. The procedure was similar to that described in previous work. The chemical composition of the samples was verified by means of scanning electron microscopy (SEM) using a LEOPard electron-probe microscope and by microanalysis using a JEOL JXA-8200 electron microscope. The crystal structure of the samples was determined by means of single crystal and powder X-ray diffraction using a high-brilliance Rájka diffractometer (Mo Kα radiation, λ = 0.7108 Å).

Single crystal X-ray diffraction under pressure. We selected high-quality single crystals of Fe3O4 and loaded them into symmetric diamond anvil cells (DACs) equipped with Boehler-Almax diamonds that enabled X-ray diffraction imaging of the entire region of angles. We employed three DACs with diamond anvil culet sizes of 400 and 300 µm. Together with the sample in the DACs, we loaded Ni as a pressure-transmitting medium. In total, we carried out three high-pressure single crystal X-ray diffraction experiments. The first one served as an initial scanning of the low-temperature phase diagram of Fe3O4, and it was performed at the ID27 beamline of the European Synchrotron Radiation Facility (ESRF, Grenoble, France) with a wavelength of λ = 0.2887 Å. Additionally, we carried out a room temperature compression experiment with laser heating at high pressures on beamline ID9a at ESRF (λ = 0.41513 Å). At each (P,T) point, we acquired one single-crystal X-ray diffraction images upon continuous rotation of the cell with the sample around the vertical c-axis with a step of Δω = 0.5° and an exposure time of t ≈ 0.5 s/frame. The diffraction data were collected using a Perkin Elmer XRD1612 detector. We analyzed these data with CrysAlisPro software, and solved the crystal structures using JANA2006 software.

We analyze the Fe–O bond lengths of all iron cations in the different crystal structures of Fe3O4 using a common BS method. In this method, a bond valence is determined as \( V_i = \sum_j \frac{d_{ij}}{b} \), where \( d_{ij} \) is the distance between atoms i and j, and \( b \) is the bond valence parameter (empirically determined for this cation-anion pair), and \( b_{\text{Fe-O}} \) is an empirical parameter about 0.37 Å, and thus, a BVs value of a cation is determined as a sum of individual bond valences \( V_i = \sum_j \frac{d_{ij}}{b} \). In these calculations, we used \( b_{\text{Fe-O}} = 0.37 \) Å and the bond-valence parameters \( b_{\text{Fe-O}} \) determined at ambient conditions for Fe2O3 and Fe3O4–O bonds as 1.734 and 1.759 Å, respectively. Using literature data from the equation of state of hematite (Fe2O3) determined from single crystal X-ray diffraction experiments up to 25 GPa, we estimated a pressure dependence of the bond parameter \( b_{\text{Fe-O}} \) for the Fe3O4–O bonds, and applied these values in the BVs estimations as well. Since the total cation charge in the formula unit (+10) should be conserved at all pressures and temperatures, the calculated nominal BVs values were accordingly renormalized to meet the charge-conservation requirement. After performing these calculations, the calculations using different starting \( R_{\text{fe}} \) values gave identical results within experimental uncertainty.

Mössbauer spectroscopy under pressure. For Mössbauer spectroscopic examination over a wide pressure–temperature range, we synthesized a polycrystalline sample of 20% Fe-enriched Fe3O4. We also utilized a membrane DAC with diamond anvil culet sizes of 400 µm. The DAC was fixed inside a cryostat. We monitored the width and the background data was subtracted using an automatic background subtraction (ARS) procedure. Field-cooling measurements of the lead and Fe3O4 samples were performed in fields of 2 mT and 0.5 T, respectively, from 300 K down to 4 K.

Data availability
The X-ray crystallographic information files (CIFs) for structures that support the findings of this study have been deposited at the Inorganic Crystal Structure Database (ICSD) with access codes 434152, 434153, 434154, 434155, and 434156. The authors declare that all other data supporting the findings of this study are available within the article and Supplementary Information files, and also available from the corresponding author upon reasonable request.

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Author contributions

S.V.O. synthesized and characterized the samples. S.V.O., M.B., E.B., K.G., A.V.K., A.S.P., and I.C. performed X-ray diffraction experiments. S.V.O. synthesized and characterized the samples. S.V.O., V.C., I. Kupenko, I. Kantor, A.I. Kostyuk, and A.S.P. assisted in the sample synthesis. S.V.O., M.B., E.B., K.G., A.V.K., A.S.P., and I.C. performed X-ray diffraction experiments at ID27 of ESRF (Grenoble, France). S.V.O. acknowledges the Sample Environment Service-HP lab and J. Jacobs for technical support of the load pool diamond anvil cells. The authors thank D. Vasilkov for contributions to the refinement of the Mössbauer spectra and their interpretation. The authors thank M. Mezouar, G. Garbarino, and A. Cairns for assistance in the structural experiments at ID27 of ESRF (Grenoble, France). S.V.O. acknowledges the financial support of the Deutsche Forschungsgemeinschaft (DFG, project # OV-110/3-1). A.A.T. was supported by the Federal Ministry for Education and Research through the Sofia Kovalevskaya Award of the Alexander von Humboldt Foundation.

Additional information

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