Jahn-Teller distortion driven magnetic polarons in magnetite

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The first known magnetic mineral, magnetite, has unusual properties, which have fascinated mankind for centuries; it undergoes the Verwey transition around 120 K with an abrupt change in structure and electrical conductivity. The mechanism of the Verwey transition, however, remains contentious. Here we use resonant inelastic X-ray scattering over a wide temperature range across the Verwey transition to identify and separate out the magnetic excitations derived from nominal Fe2⁺ and Fe3⁺ states. Comparison of the experimental results with crystal-field multiplet calculations shows that the spin-orbital dd excitons of the Fe2⁺ sites arise from a tetragonal Jahn-Teller active polaronic distortion of the Fe2⁺O₆ octahedra. These low-energy excitations, which get weakened for temperatures above 350 K but persist at least up to 550 K, are distinct from optical excitations and are best explained as magnetic polarons.

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Since its first X-ray structural elucidation by Bragg in 1913 and the discovery of the Verwey transition23 in magnetite ($\text{Fe}_3\text{O}_4$), it has received much attention for decades. Even today, it attracts significant scientific and technological interest for its applications in ultrafast magnetic sensors4, palaeomagnetism5, nanomedicine carriers6, and so on. Fe$_3$O$_4$ becomes magnetically ordered below $T_V \approx 850$ K. Because previous results of optical conductivity23 and X-ray absorption-energy centroid of Fe$^{2+}$ agree that the charge disproportionation involves changes in the magnetic moments of Fe$^{2+}$ and Fe$^{3+}$ states associated with the Jahn-Teller distortion. Verwey first suggested a Fe$^{2+}$–Fe$^{3+}$ charge-ordering occurring on the B-sites as the driving force of this transition. There are two major schools of interpretation: the first one interprets the Verwey transition as a transition driven by charge/orbital ordering7–17. The second one exploits the mechanism of a lattice distortion-driven electron–phonon coupling18–22 enhanced by the on-site Coulomb interaction19 and thus opens a gap at the Fermi level when the temperature is lowered below the Verwey transition temperature $T_V$.

Although numerous investigations have been carried out to verify the charge localization on the B-sites, the charge-ordering pattern of magnetite is subtle and still elusive19,20. While it is agreed that the charge disproportionation involves changes in the nominal Fe$^{2+}$ and Fe$^{3+}$ states associated with the B-sites, X-ray diffraction studies of the low-temperature phase of magnetite microcrystals15,17 revealed that the $t_{2g}$ electrons of the B-sites are not fully localized in the form of Fe$^{3+}$ states. Instead, the electrons are distributed over linear three-Fe-site units termed trimerons, which are coupled to the $T_J$ Jahn-Teller distortion of B-site Fe$^{2+}$–O$_6$ octahedra, as illustrated in Fig. 1. To the first approximation, the B-site Fe$^{3+}$–O$_6$ octahedra are Jahn-Teller inactive. The tetragonal distortion of B-site Fe$^{2+}$–O$_6$ octahedra removes the degeneracy of $t_{2g}$ orbitals, in going from $O_h$ symmetry to $D_{4h}$ symmetry. In the absence of spin–orbit coupling, an effective energy separation $\Delta_{t_{2g}}$ between $d_{xy}$ and $d_{yz}/d_{zx}$ is created if the four Fe–O bonds in the $xy$ plane are elongated or contracted. The trimeron scenario then indicates that the Verwey transition is essentially due to an ordering of trimerons. Because previous results of optical conductivity23 and photoemission24–27 showed the pseudogap feature of magnetite above $T_V$, and results of entropy analysis16, neutron/X-ray diffuse scattering28 and anomalous phonon broadening22 revealed the short-range order above $T_V$, one important open question is whether trimeron correlations persist in the cubic phase at temperatures above $T_V$. Combining these short-range correlations of polaronic characters with the spin degrees of freedom of $t_{2g}$ electrons, one can expect magnetic polarons in magnetite.

Here we present measurements of resonant inelastic X-ray scattering (RIXS)$^{30,31}$ at the Fe $L_\gamma$-edge on magnetite to reveal the low-energy spin–orbit excitations of Fe$^{2+}$ ions in both the monoclinic and cubic phases. To the best of our knowledge, the magnetic excitations derived from the local tetragonal distortion field of Fe$^{2+}$ ions, that is, magnetic polarons, have not been reported to date. In combination with crystal-field multiplet calculations, we show the existence of magnetic polarons in magnetite which is driven by the Jahn–Teller distortion.

Results

Fe $L_\gamma$-edge RIXS. Figure 2a shows the Fe $L$-edge X-ray absorption spectrum of magnetite. By comparing with crystal-field multiplet calculations (see Supplementary Fig. 1), it is understood that the absorption-energy centroid of Fe$^{2+}$ ions is lower than that of Fe$^{3+}$ ions by $\sim 1$–2 eV, consistent with earlier work$^{32–34}$. Accordingly, the features at X-ray energies of 706.0 and 707.5 eV originate from the absorption of octahedrally coordinated B-site Fe$^{2+}$ states, while the maximum intensity feature at 708.8 eV is dominated by absorption from the Fe$^{3+}$ ions of both the B-site octahedral and A-site tetrahedral symmetries.

The colour map of RIXS intensity measured at 80 K in the plane of incident photon energy versus energy loss shown in Fig. 2b presents the evolution of the RIXS spectral profile associated with Fe$^{2+}$ and Fe$^{3+}$ as detailed in the following. When the incident X-ray energy was set to below 707.5 eV, we observed $\delta d$ excitations of Fe$^{2+}$ with energy losses at $2.8 \pm 0.5$, $1.65 \pm 0.05$ and $1.16 \pm 0.05$ eV shown in Fig. 2c, and also a broad excitation centred at 200 meV shown in Fig. 2d. If the incident X-ray energy goes beyond 707.5 eV, the 1.16-eV $\delta d$ excitation of Fe$^{2+}$ begins to evolve into a fluorescence that has a constant X-ray emission energy independent of incident energy. With the incident X-ray energy set to 708.8 eV, RIXS excitations arise mostly from Fe$^{3+}$ ions of octahedral or tetrahedral symmetry. Figure 2d shows two RIXS features centred at 90 and 200 meV in a magnified plot of energy loss below 0.7 eV. Measurements carried out by varying the scattering angle suggested that these two low-energy excitations do not disperse in momentum space (see Supplementary Fig. 2). The 200-meV excitation has a full-width at half-maximum larger than the instrumental energy resolution. This broad RIXS feature resonates near the $L_\gamma$-edge of Fe$^{2+}$ and almost disappears for incident energy above 708 eV, at which the other excitation centred at 90 meV emerges. The 90-meV excitation has a full-width at half-maximum nearly equal to the instrumental energy resolution and resonates at 708.4 eV. The distinct incident X-ray energies for these resonant excitations indicate that the 200- and 90-meV features arise from Fe$^{2+}$ and Fe$^{3+}$ states, respectively.

Many experimental$^{35–37}$ and theoretical$^{30,38–41}$ studies have shown that $L$-edge RIXS allows spin–flip processes that are not accessible with optical spectroscopy$^{23}$. For example, if both the incident and scattered X-rays are $\pi$-polarized, the spin–flip excitation of $d_{xz}$ is allowed owing to the spin–orbit coupling in the $2p$ core state. In the present RIXS measurements with a 90°-scattering geometry (see Supplementary Fig. 2a), the intensity of elastic excitation with incident X-rays of $\pi$ polarization is reduced in comparison with that of $\sigma$ polarization, and spin–flip excitations are effectively revealed. In addition, the cross-section...
of \( L_3 \)-edge RIXS for a magnetic excitation is usually larger than that for a phonon excitation. Because \( O \) \( K \)-edge RIXS-probe excitations derived from bimagons and phonons, we performed \( O \) \( K \)-edge RIXS measurements to probe the phonons of \( Fe_3O_4 \). Our data shown in Supplementary Fig. 4 reveal an excitation at 70 meV in the \( O \) \( K \)-edge RIXS, indicating that the observed 90-meV feature of the \( Fe \) \( L_3 \)-edge RIXS has a small contribution from phonon excitation.

**Multiplet RIXS calculations.** In order to characterize the origin of the observed excitations, we undertook crystal-field multiplet calculations for the \( B \)-site \( Fe^{3+} \) and \( Fe^{2+} \) ionic configurations. See the Methods section, Supplementary Note 2 and Supplementary Figs 5 and 6 for calculation details.

Multiplet calculations carried out for the \( B \)-site \( Fe^{3+} \) ions under an exchange magnetic field of 90 meV, as shown in Supplementary Fig. 5d, explain the observed excitation energy of 90 meV well. This is consistent with the 100-meV Zeeman splitting induced by the molecular field deduced from the Curie temperature of magnetite and the exchange coupling constants. This spin–flip energy also agrees with the energy of the nearly 90-meV RIXS feature can change under a spin reorientation as the experimental resonance starts at an energy lower than that of the resonant quasi-elastic scattering of \( Fe^{2+} \) and its energy range is broad, while the calculated resonance starts at a higher energy with a narrow range. This discrepancy is attributed to differences in the dynamics of 3d orbitals due to core–hole effects in intermediate states. These effects do not affect the energy loss of excitation spectra because the core holes are filled in the RIXS final state. As is typical of RIXS calculations reported in the literature, our calculations do not include such core–hole effects, and hence do not reproduce the incident energy dependence perfectly, but our calculations correctly reproduce the energy-loss features.

**Discussion**

In comparison with the magnified intensity map of RIXS measurements shown in Fig. 3b, calculations using a molecular field \( H_{ex} = 90 \) meV and \( \Delta_{t_{2g}} = -22 \) reproduce the energy-loss features. For the 200-meV excitation, the experimental resonance starts at an energy lower than that of the resonant quasi-elastic scattering of \( Fe^{2+} \) and its energy range is broad, while the calculated resonance starts at a higher energy with a narrow range. This discrepancy is attributed to differences in the dynamics of 3d orbitals due to core–hole effects in intermediate states. These effects do not affect the energy loss of excitation spectra because the core holes are filled in the RIXS final state. As is typical of RIXS calculations reported in the literature, our calculations do not include such core–hole effects, and hence do not reproduce the incident energy dependence perfectly, but our calculations correctly reproduce the energy-loss features.

Figure 3c presents calculated RIXS spectrum in comparison with measurements of the incident X-ray energy set to 707 eV, at which the 200-meV RIXS feature is most pronounced. The negative value of \( \Delta_{t_{2g}} \) signifies that the energy of \( d_{yz} \) is lower than that of \( d_{zx} / d_{z^2} \) that is, tetragonally distorted \( Fe^{2+} \) octahedra with elongated \( Fe=O \) bonds in the \( xy \) plane. This shows that the tetragonal distortion is directly related to a polaronic distortion of...
the Fe$^{2+}$O$_6$ octahedra, which in turn couple to the neighbouring Fe$^{3+}$O$_6$ octahedra constituting the trimerons, although, as mentioned earlier, they are Jahn-Teller-inactive in the first approximation. Our results are consistent with the locally distorted structure of the FeO$_6$ octahedra and the short-range order above $T_V$ observed by X-ray absorption and diffuse scattering. These short-range correlations are polaronic in nature and a tetragonal Jahn-Teller polaronic distortion are required to correctly simulate the excitation energy, the observed spin–orbital excitations are, indeed, magnetic polarons.

The magnitude of obtained $\Delta_{t_{2g}}$ is comparable with the 3d spin–orbit coupling strength, and thus confirms the observation of the unquenched orbital moment, which is known from work on Fe$^{2+}$ impurities in MgO thin films. These results are also consistent with conclusions of band-structure calculations using the monoclinic P$2_1/c$ crystal structure of magnetite (see Supplementary Note 3 and Supplementary Fig. 7), which give an energy splitting $\Delta_{t_{2g}}$ between minority-spin $d_{xy}$ and $d_{yz}/d_{zx}$ bands at the $\Gamma$ point, conforming to the deduced $\Delta_{t_{2g}}$.

We also performed RIXS measurements above the Verwey transition and found that the spin–orbital excitations driven by polaronic distortion do exist in the cubic phase of Fe$_3$O$_4$ at high temperatures as shown in Fig. 2e and Supplementary Fig. 8. Figure 4 plots the temperature-dependent RIXS spectra with the incident X-ray energy set to the pre-edge absorption at 706 eV, an incident X-ray energy at which the elastic component is weak and the RIXS arises predominantly from octahedral Fe$^{2+}$ ions with a negligible contribution from Fe$^{3+}$. The temperature-dependent results show that, when the temperature is varied across $T_V$, the spin–orbital excitation of 200 meV does not abruptly change its intensity and persists at least up to 550 K, albeit with a gradual decrease above 350 K. We interpret this as a gradual weakening of the polarons. RIXS results shown here serve as a fast probe to snapshot the dynamic lattice–spin–orbital excitations of Fe$_3$O$_4$.

These temperature-dependent RIXS results indicate that the FeO$_6$ octahedra are already locally distorted in the cubic phase of magnetite, in good agreement with the existence of the short-range correlations in the lattice structure above $T_V$. The temperature dependence of these distortions follows that of the magnetization of magnetite, suggesting short-range ordering of the Jahn-Teller distortion, which gets weakened as the temperature approaches the Curie temperature $T_C$, and providing further evidence for magnetic polarons. These observations suggest that the local distortion in the cubic phase could be attributed to the precursor of the monoclinic phase across the Verwey transition.
To summarize, our results demonstrate the usefulness of RIXS to unravel the local electronic structure of a mixed-valence compound by selecting the energy and polarization of incident X-rays. We revealed nd excitons in magnetite that have an energy centroid 200 meV and arise from polaronic distortion-driven spin–orbital excitations, which are best explained as magnetic polarons. We also applied crystal-field multiplet calculations to obtain the $t_{2g}$ crystal field $\Delta_{T_2} = -26 \pm 4$ meV induced by the tetragonal Jahn–Teller distortion. These results are consistent with the mechanism of ordering trimerons for the Verwey transition. It would be interesting to carry out RIXS experiments with an improved energy resolution to study the change of spin–orbital excitations across the Verwey transition.

**Methods**

**RIXS measurements.** Using the AGM–AGS spectrometer at beamline 05A1 of the Taiwan Light Source, we measured RIXS on a single-crystal Fe$_2$O$_3$(001) at incident photon energies set to specific energies about the $L_2$(2p$_{3/2}$→3d) absorption edge of Fe. See Supplementary Fig. 2a for the scattering geometry. Both the scattering angle $\phi$ defined as the angle between the incident and the scattered X-rays, and the incident angle $\theta$ from the crystal ab plane, were variable. The polarization of the incident X-ray was switchable between $\sigma$ and $\pi$ polarizations, that is, the polarization within and perpendicular to the scattering plane, respectively, and the polarization of scattered X-rays was not analysed. The energy bandwidth of the incident X-rays was 500 meV, and the total RIXS energy resolution was $\sim$80 meV because the energy compensation method was used to ensure a high-resolution measurement in the energy-loss scheme. The beam diameter of incident X-ray at the sample is $\approx 0.5$ mm.

**Sample preparation.** Single-crystal growth of magnetite was carried out in an infrared image furnace in high-purity argon gas (99.999% purity) atmosphere. Measurements of the temperature-dependent specific heat and resistivity of the magnetite are available in Supplementary S12 and Supplementary S13. Indicative of a nearly ideal chemical stoichiometry. See Supplementary Figs 10 and 11 for the sample characterization.

**Multiplet calculations.** We undertook crystal-field multiplet RIXS calculations of B-site Fe$^{2+}$ and Fe$^{3+}$ using CTM4RIXS and MISSING (Dallera and Gusmeroli [http://www.esrf.eu/computing/scientic/MISSING]) with the scattering angle 90° and the magnetization axis perpendicular to the scattering plane or in the scattering plane with angles 20° or 70° to the incident beam. The polarization of incident X-rays was set to $\pi$-polarized, indicative of a nearly ideal crystal-field geometry. See Supplementary S12 and Supplementary S13 for the sample characterization.

**Data availability.** The data that support the findings of this study are available from the corresponding authors on request.

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**Author contributions**

All authors made significant contributions. H.Y.H., Z.Y.C., W.B.W., J.O. and A.S. performed RIXS measurements. H.Y.H., R.P.W. and F.M.F.d.G. performed multiplet calculations. H.-J.I. and G.Y.G. performed band-structure calculations. C.T.C. designed the RIXS beamline and spectrometer. Z.-Y.L. and J.-S.Z. synthesized and prepared the magnetite single crystals. D.J.H., H.Y.H., F.M.F.d.G., A.C., J.-S.Z., J.-G.P. and L.H.T. analysed the data, discussed the results and wrote the paper. D.J.H. is responsible for project planning.

**Additional information**

**Supplementary Information** accompanies this paper at http://www.nature.com/naturecommunications

**Competing interests:** The authors declare no competing financial interests.

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